

AL/EQ-TR-1995-0013
VOL I



**DEMONSTRATION AND EVALUATION OF THE AIR FORCE SITE
CHARACTERIZATION AND ANALYSIS PENETROMETER SYSTEM
IN SUPPORT OF NATURAL ATTENUATION INITIATIVES
VOLUME I - SYSTEM DEVELOPMENT AND
EVALUATION**

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February 1996

Final Technical Report for Period October 1993 - December 1994

Approved for public release; distribution unlimited.

**AIR FORCE MATERIEL COMMAND
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REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT AVAILABLE FOR PUBLIC RELEASE DISTRIBUTION UNLIMITED		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 5868			5. MONITORING ORGANIZATION REPORT NUMBER(S) AL/EQ-TR-1995-0013 Vol I		
6a. NAME OF PERFORMING ORGANIZATION APPLIED RESEARCH ASSOCIATES, INC.		6b. OFFICE SYMBOL (If applicable) ARA	7a. NAME OF MONITORING ORGANIZATION ARMSTRONG LABORATORY ENVIRONICS DIRECTORATE		
6c. ADDRESS (City, State, and ZIP Code) RFD #1, BOX 120A WATERMAN ROAD SOUTH ROYALTON, VT 05068			7b. ADDRESS (City, State, and ZIP Code) AL/EQ-OL 139 Barnes Drive Suite 2 TYNDALL AFB, FL 32403-5323		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F08635-93-C-0020		
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
					WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Demonstration and Evaluation of the Air Force Site Characterization and Analysis Penetrometer System in Support of Natural Attenuation Initiatives. Volume I - System Development and Evaluation (Volume I of V)					
12. PERSONAL AUTHOR(S) Martin L. Gildea, Wesley L. Bratton, Ph.D., James D. Shinn, II, P.E.,					
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM 10/93 TO 12/94		14. DATE OF REPORT (Year, Month, Day) 960209	
15. PAGE COUNT					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>A second-generation tunable Laser-Induced Fluorescence-Cone Penetrometer Test (LIF-CPT) system has been developed and demonstrated at three different Air Force Bases as an alternative site characterization technology. This represents an innovative technology for delineating soil contamination resulting from fuel spills. Applied Research Associates, Inc. and Dakota Technologies, Inc. jointly conducted the system development and demonstration project. Demonstrations consisted of 2-week efforts at each of Air Force Bases: Plattsburgh Patrick/Cape Canaveral, and Dover. The data collected during these demonstration supported both evaluation of the LIF-CPT systems along with support for selecting a site for a natural attenuation experiment the Air Force is [planning. Data analysis indicates that the second generation system is operationally improved over the first-generation system and has improved detection capabilities. The improved detection capability is related to a new optical module used to focus laser light and filter the return signal to reduce the signal-to-noise ratio. Although the system is improved in many ways, some questions still exist concerning the influence soil type has had on some of the system responses. Further analysis is required to resolve these discrepancies.</p>					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION /		
22a. NAME OF RESPONSIBLE INDIVIDUAL Bruce Nielsen			22b. TELEPHONE (Include Area Code) (904) 283-6227		22c. OFFICE SYMBOL EQW-OL

PREFACE

This report was prepared by Applied Research Associates, Inc. (ARA), 120-A Waterman Road, South Royalton, VT 05068 under U. S. Air Force Contract No. F08635-93-C-0020, SSG Subtask 8.01.1 for the Armstrong Laboratory Environics Directorate, AL/EQW-OL, 139 Barnes Dr. Suite 2, Building 1120, Tyndall AFB, FL 32403-5323.

This final report discusses the continued development of the combined technology of the cone penetrometer (CPT) and laser-induced fluorescence (LIF) as it pertains to the detection and quantification of petroleum oils and lubricants (POL's) within subsurface soils environments. Specifically the report covers a review of LIF-CPT technology; LIF-CPT system specifications; evaluation of the LIF-CPT probe under field conditions; and LIF data analysis/evaluation. The data and results of the field investigations were subsequently used to determine if bioventing or natural attenuation approaches are viable remedial alternatives at three U.S. Air Force Bases.

The work was performed between October 1993 and December 1994. The AL/EQW project officer was Mr. Bruce Nielsen.

EXECUTIVE SUMMARY

A. OBJECTIVE

Applied Research Inc. (ARA) and Dakota Technology, Inc. (DTI) were retained by the Armstrong Environics Directorate AL/EQ-QL to further develop laser-induced fluorescence-cone penetrometer technique (LIF-CPT) for use during environmental site investigations. The primary objective of the program was to develop and evaluate an improved LIF-CPT system for the characterization of fuel-contaminated sites. The evaluation was based on the results from demonstrations, testing and evaluation at three Air Force bases. A parallel goal of the demonstrations was to gather data for Engineering-Science, Inc. (E-S) to determine if bioventing or natural attenuation are viable alternatives for remediating numerous Air Force sites.

B. BACKGROUND

The Department of Defense (DoD) is seeking efficient and cost effective means to assess, remediate, and monitor petroleum-contaminated and hazardous waste sites at both active and decommissioned installations. The Air Force's Installation Restoration Program Information Management System (IRPIMS) database lists approximately 1,400 fuel-contaminated sites and 300 inactive firefighter training facilities; presently the IRPIMS database contains data from only one-half of the installations. Current environmental site investigations based on drilling technology are slow, expensive and potentially dangerous. Cone penetrometer (CPT) based investigations, on the other hand, allow real-time data collection and don't produce soil cuttings thus eliminating disposal costs and health and safety risks due to exposure.

Cone penetrometer testing gathers accurate in situ geotechnical information in a rapid and cost-effective manner. With adaptation of in situ geophysical and chemical sensors to the cone penetrometer probe, subsurface hydrogeology and the extent of contamination can be mapped simultaneously. The speed and continuous nature of the information generated by LIF-CPT reduces the need for costly and invasive subsurface sampling and installation of long term monitoring wells.

C. SCOPE

To fulfill the objectives of this project, the following tasks were completed; (1) Development, fabrication and integration of a field-deployable, wavelength-tunable LIF system, (2) Laboratory testing and evaluation of the LIF system, (3) Demonstration, testing and evaluation programs at Plattsburgh, Patrick/Cape Canaveral, and Dover Air Force Bases (AFB's), and (5) Delivery of a completed LIF system to the U. S. Army Corp. of Engineers.

Extensive evaluation and calibration of the LIF-CPT remained outside of the scope of this project. Such a study could not be completed during this project due to the dual objectives of

developing the LIF-CPT, and employing the tool and other CPT capabilities on a production basis for the engineering-cost evaluation conducted by E-S.

D. METHODOLOGY

The United State Army Corp of Engineers Waterways Experimental Station (USAE WES) initially developed the LIF-CPT using a mercury lamp as an excitation source downhole within the cone. The resulting fluorescence was collected and directed to a detection system located in the cone penetrometer truck via a single optical fiber. WES soon eliminated the mercury lamp in favor of a pulsed laser source external to the cone; a nitrogen laser system, limited to the emission of a single excitation wavelength of 337 nanometer (nm) was employed. This was useful for the detection of large multi-ring fuels such as Diesel Fuel Marine (DFM) but proved ineffective for "lighter" fuels such as jet fuels and gasoline which require excitation at shorter wavelength. Further research sponsored by the Air Force concluded that a tunable wavelength, pulsed laser (Nd:YAG) with a fiber optic probe and detection system would satisfy the needs of the Air Force. During the scope of the current program Applied Research Associates, Inc., in cooperation with Dakota Technology, Inc. (DTI), refined the Nd:YAG pulsed LIF-CPT system and demonstrated its utility in the field.

E. TEST DESCRIPTION

The test program consisted of two phases; (1) redesign and build a new laser system based on the findings of a previous LIF-CPT development program, and (2) evaluation of the LIF-CPT system under field conditions at three Air Force Bases. The redesign of the LIF-CPT system consisted of two major efforts: (1) optimizing the overall laser system performance by upgrading individual components with state-of-art components and repackaging the system improving portability and durability, (2) redesign the LIF-CPT probe to maximize the performance and durability and minimize cost. During the field demonstration and evaluation program several objectives were addressed. The primary technical focus was to evaluate the LIF-CPT system in the field for reliability, stability and repeatability, correlation of LIF-CPT intensity to contaminate concentration and evaluation of the sources of data scatter in the chemical and LIF-CPT data.

F. RESULTS

During the three demonstrations the laser system performed quite well. Many of the system improvements greatly enhanced both field utility and system stability. Minor improvements are still needed to enhance power stability, although the recording of the current power levels is highly beneficial.

Evaluation of the LIF response shows that there are effects related to both the soil type and moisture content of the materials being tested. The effect of soil type is fairly significant, since at some locations no LIF response was recorded in visibly contaminated clay samples. The effect of

moisture content is minimal. Further investigation into these responses would be highly beneficial. Finally, the limited data sets available permitted only speculation about possible correlations between LIF response and to be performed. The results from the statistical analysis are encouraging and additional testing performed.

G. CONCLUSIONS

In general the LIF and chemical analytical data agree well qualitatively. Evaluation of the limited chemical and LIF data indicates that there may be a correlation between total BTEX and Xylene concentrations and LIF response. The background limit of the LIF response was determined to be independent of the soil type but may have a weak dependency on moisture content. The background limit of the current LIF-CPT probe configuration is approximately 50 counts. There are still some unanswered questions regarding the response of the LIF system in different soils. Areas known to be highly contaminated showed little or no response in fine grained soils (e.g., silts and clays). Insufficient chemical data was available to fully validate the LIF system.

H. RECOMMENDATIONS

Additional data collection and evaluation is required to fully validate the LIF-CPT system. For future testing, it is strongly recommended that on-site analytical screening for Total Petroleum Hydrocarbons (TPH) by EPA method 418.1 be conducted on soil samples. This data can subsequently be used to correlate TPH concentration to LIF response. Combining objectives that include production-oriented data collection for other research is not recommended.

I. APPLICATION

The LIF-CPT system can be implemented by the Air Force as the primary technology to conduct environmental site assessments where petroleum, oils and lubricants are the contaminants of interest. It could be used both as an initial screening tool and/or as a tool to monitor the effectiveness of a particular remedial effort.

J. BENEFITS

Significant reductions in the time and cost of conducting environmental site assessments could be realized by implementing the LIF-CPT technology. This system provides superior data in real-time to use as a basis for selecting an appropriate remedial strategy.

K. TRANSFERABILITY OF TECHNOLOGY

Virtually all industrial contractors involved with subsurface environmental site assessments where petroleum oils and lubricants are concerned could profit from the use of LIF-CPT technology. The industry in general is constantly seeking ways to conduct business faster, cheaper, and better; CPT-LIF fulfills these criteria.

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SECTION I INTRODUCTION

A. OBJECTIVE

The Air Force Site Characterization and Analysis Penetrometer System (AFSCAPS) project combines technology from the Tri-Services Site Characterization and Analysis Penetrometer System (SCAPS) program and the Air Force's Tunable Laser Spectroscopy Program. AFSCAPS was initiated to rapidly transition the combined technology to Air Force service agents to enable them to address characterization, remediation and postremedial monitoring of fuel-contaminated sites in a more efficient and effective manner.

The primary program objective was to develop and evaluate an improved Laser-Induced Fluorescence-Cone Penetrometer Technique (LIF-CPT) system for the characterization of fuel-contaminated sites. The evaluation was primarily based on the results from demonstrations at three Air Force bases. A parallel goal of the demonstrations was to determine if bioventing or natural attenuation are viable alternatives for remediating numerous Air Force sites.

B. BACKGROUND

The Department of Defense is conducting nationwide remediation efforts to clean up contaminated military and weapons facilities. It is estimated that remediation of these DOD sites will require the expenditure of \$24 billion dollars by the DOD over the next 30 years. Identifying, characterizing and developing remediation plans for these contaminated sites are high priorities for the DOD.

The Air Force seeks efficient methods to assess, remediate, and monitor petroleum-contaminated and hazardous waste sites at both active and decommissioned installations. Jet fuels such as JP-4, JP-5 and JP-8 are the most common fuels to be stored, transferred and consumed, although other fuel spills such as heating oil, diesel fuel, and gasoline are also of concern. Typical jet-fuel contaminated sites at Air Force installations include fuel storage and transfer facilities, fuel purge areas, and firefighter training facilities. The Air Force's Installation Restoration Program Information Management System (IRPIMS) database lists approximately 1,400 fuel-contaminated sites and 300 inactive firefighter training facilities. The database contains information from only one-half of the installations.

Cone Penetrometer Testing (CPT) gathers accurate in situ geotechnical information in a rapid and cost-effective manner. With the adaptation of in situ geophysical and chemical sensors to the cone penetrometer probe, subsurface contamination can be mapped simultaneously. CPT minimizes waste generation and the exposure of field personnel to hazardous environments, compared to traditional drilling methods where the borehole is open to the atmosphere. High waste management costs generated from the handling and disposal of contaminated soils (drilling waste) are also eliminated. The speed and continuous nature of the Laser-Induced Fluorescence (LIF)-CPT information reduce the need for costly and invasive subsurface sampling and installation of long term monitoring wells.

The potential for substantial cost savings realized through cone penetrometer-based environmental site investigations has fostered collaborative federal research and development efforts by the U.S. Army, Navy and Air Force in a program known as the Site Characterization and Analysis Penetrometer System (SCAPS). SCAPS generically refers to chemical sensors deployed with a cone penetrometer. Much of the SCAPS work to date employs fiber-optic-based spectroscopy with light delivered to the soil via a sapphire window "viewport" in the side of the cone. Sapphire (a crystalline phase of Al_2O_3) is too hard to be scratched by sand and other materials encountered as the cone is pushed through the soil. The sapphire window concept was developed and first implemented by personnel at the U.S. Army Corps of Engineers Waterways Experiment Station (WES) (Reference 1).

The WES group initially used a mercury lamp downhole in the cone for excitation and returned the fluorescence to a detection system in the cone penetrometer truck via a single optical fiber. However, the mercury lamp was eliminated in favor of a pulsed laser source external to the cone. The source light was delivered to the sapphire window with a separate excitation fiber. The spectroscopic unit is patterned after the nitrogen laser source and optical multichannel analyzer (OMA) detector developed at the Naval Command, Control and Ocean Surveillance Center (NCCOSC). Technical details were reported at the 1991 Field Screening Symposium (Reference 2) and there have only been minor design changes in the interim. The output wavelength of the nitrogen laser (337 nm) makes it most appropriate for detection of "heavier fuels" such as diesel and diesel fuel marine (DFM).

The Air Force's interests are primarily in "lighter" fuels (i.e., those with a hydrocarbon distribution shifted to lower molecular weights). To complement the WES SCAPS work, the Air Force has sponsored laser spectroscopy research at North Dakota State University (NDSU). In particular, the Air Force research at NDSU led to a laser fluorimeter to analyze aromatic

hydrocarbons in solution and neat fuel. The NDSU system features a wavelength-tunable dye laser pumped by a pulsed Nd:YAG laser, fiber-optic probe and cable, and detection system. This system provides excitation wavelengths shorter than the nitrogen laser system used by WES in the SCAPS program. The lighter fuels, such as jet fuels and gasoline, can be excited and detected with the shorter excitation wavelengths.

The active investigation LIF technology, as applied to the environmental field, began in the mid 1980s. In 1983, T. Hirschfeld (Reference 3) first proposed that fluorescent dye tracers be monitored with fiber-optics in the visible wavelength range. He also suggested that classic Raman spectrometers be used to monitor the fluorescence because of their fluorimeter-like design and higher overall efficiency in dealing with low power signals.

The first report of fiber-optic fluorescence spectroscopy for analysis of aromatics in water was the 1985 publication of Chudyk, Carrabba, and Kenny (Reference 4). They used the frequency-doubled output of a nitrogen-pumped dye laser (270 nm) or the fourth harmonic of a Nd:YAG laser (266 nm) as their excitation source. A fiber-optic probe with two 600-micrometers fused silica fibers was used. One fiber delivered the laser light to the sample and the other carried the fluorescence to a photomultiplier tube (PMT). The signal from the PMT was monitored with a boxcar integrator. Considerable effort was made by Chudyk et al. (Reference 4) to analyze launch efficiencies, fiber losses, and damage thresholds for the excitation beam. No attempt was made by the authors to incorporate time resolution into the technique. Lieberman et al. (Reference 5) developed a pulsed-laser, fiber-optic-based fluorimeter to determine fluorescence decay times of polynuclear aromatic hydrocarbons (PAHs) in sea water. They use pulsed nitrogen laser excitation with an intensified diode array detector. Lifetimes are measured by advancement of the detector gate, which is about 5 ns wide. The fiber probe used contains a 2 meter long bifurcated seven-fiber bundle (six-around-one probe), each with a core diameter of 325 μ m. A 10 meter length of 325 μ m fiber delivers the light from the laser to the central fiber of the bundle. Much of Lieberman's focus has been on diesel fuel marine (DFM), a fuel widely used by the Navy. DFM contains significant quantities of larger PAHs, such as anthracene and benzo[a]pyrene. The data they reported was for these species dissolved in a solvent mixture of air-saturated sea water and a small volume of ethanol. This is the genesis of the system incorporated into the SCAPS program at WES and used by the Navy, who began operating their own SCAPS vehicles in 1993.

The initial work and much of the current work is centered on developing a field-portable LIF system that can be used in situ to supplement and, in the future, replace analytical testing. Research in this field has demonstrated the fluorescence characteristics of a wide range of fuel

compounds. Common chemical contaminants such as the chlorinated hydrocarbons (TCE, PCE) are known not to fluoresce and are not a candidate for the LIF technique. As demonstrated by Chudyk, et al. (Reference 4), Lieberman, et al. (Reference 5), and Gillispie and St. Germain (Reference 6), common fuel contaminants such as heating oil, jet fuels, gasoline, and DFM exhibit strong fluorescence signatures, with the degree of fluorescence dependent upon the excitation wavelength. Large multiring fuels, such as DFM, will fluoresce when excited with long wavelength excitation sources, such as the 337-nanometer (nm) nitrogen laser used in the SCAPS system. Lightweight fuels, such as jet fuels and gasoline, have weak spectral signatures when excited with a 337-nm light pulse. Excitation at shorter wavelengths, such as 280 to 290 nm for jet fuels and 260 nm for gasoline, provide stronger and distinctive fluorescence spectra. Another limitation of shorter wavelength operation is the increased light attenuation as compared to the longer wavelength 337 nm laser. A tunable laser, as demonstrated on this project, allows the investigator to select the most appropriate wavelength for contaminant of interest and site conditions. This was the motivating force behind the NDSU laser system.

The original AFSCAPS project was initiated to transition the combined technology of the SCAPS program and the Air Force Laser Spectroscopy Program to Air Force service agents. This work was accomplished by installing the NDSU laser system in an Applied Research Associates, Inc. (ARA) cone penetrometer vehicle and implementing the system using the fiber-optic cone concept from WES. This system was demonstrated at Tinker AFB during August 1992. Results from this program are documented by Bratton, et al., 1993 (Reference 7). The goals of the program were to develop, demonstrate, and evaluate an improved LIF-CPT system for the characterization of fuel contaminated sites. Jet fuels were the primary interest, although limited testing of gasoline contaminated soils was conducted. The LIF-CPT was used in three 10-day field demonstration programs at Plattsburgh AFB, Patrick AFB/Cape Canaveral AFB and Dover AFB to gather data for an Engineering Evaluation/Cost Analysis to determine the feasibility of bioventing and/or natural attenuation as a remedial alternative. A secondary goal was the collection of data for system evaluation.

C. SCOPE

To fulfill the objectives of this project, the following tasks were completed:

- Evaluation of the current state of the art and development of specifications for a field-deployable, wavelength-tunable LIF system,
- Fabrication and integration of the LIF system in ARA's CPT truck,
- Laboratory evaluation testing,

- Preparation of Demonstration, Test and Evaluation (DT&E) Plans for Plattsburgh, Patrick /Cape Canaveral, and Dover Air Force Bases (AFB),
- Performance of the DT&E programs at each of the air bases, and
- Delivery of a completed LIF system to the U. S. Army Corp. of Engineers.

D. ORGANIZATION

Section II of this volume provides a review of laser-induced fluorescence sensing capabilities and a related discussion on measurements technology in soils. Section III contains a description of the system specifications including a discussion of improvements over the Tinker system, probe design, and operation of the LIF-CPT system. Section IV presents the testing procedures used for both the LIF-CPT and sampling activities during each of the DT&E's and a description of all testing performed at each base. Included in Section V are detailed analyses of the LIF-CPT data and the development of correlations to contaminant levels. Section VI contains conclusions and recommendations regarding the LIF-CPT system.

Volumes II, III, and IV contain the data collected from each of the demonstrations and includes site plans, LIF-CPT logs, LIF multidimensional analyses, and chemical data. Section II of Volume II presents a detailed discussion of the theory and application of CPT technology. The Operation and Maintenance Manual is included as Volume V.

SECTION II

TECHNOLOGY REVIEW

A. INTRODUCTION

Fiber-optic spectroscopy is a promising approach to in situ analysis of fuels, solvents, and other chemical species. In conventional spectroscopic analysis, the sample must be transported to the instrument (spectrometer). Using fiber-optic methods, light is transported to the sample and subsequently returned to the detector with fiber-optics. Measurements can be made in situations where grab sampling would be extremely difficult or even impossible.

There are two principal forms of fiber-optic spectroscopy. In the direct method, the fiber functions essentially as a "light pipe" between the spectrometer and the instrument. The other method utilizes fiber-optic chemical sensors (optrodes), where the interaction between an analyte and a reagent immobilized on the fiber affects the light signal passing through the fiber. Optrode approaches generally rely on relatively simple optical instrumentation. The desired sensitivity and specificity must come from the chemistry of the reagent-analyte interaction.

Implementation of optrodes into cone penetrometer testing is far less promising than the direct method. Optrodes require intimate contact between the sensing device (fiber) and the sample. If the active region of the optrode is placed on the outside surface of the cone, it will likely be destroyed almost immediately as the cone is advanced into the subsurface. An alternative configuration requires sample mass transport from outside the cone to an optrode placed inside. Such schemes could be used to monitor soil gas or groundwater samples; however, they are limited to static measurements while the cone is stopped. Measurement of continuous concentration profiles while the cone is being advanced is difficult because:

- the reagent-analyte chemistry is too slow,
- mass transport of the analyte into the cone is too slow, and
- there is sample carryover as the cone advances from a region of high contamination to much lower concentrations.

Direct fiber-optic approaches are relatively straightforward to implement and represent the thrust of this work. The principal direct fiber-optic spectroscopies are absorbance, fluorescence, and Raman scattering. This review emphasizes fluorescence measurements, because fluorescence is the easiest and oldest of the three to be accomplished with CPT. The experimental approach to

Raman scattering is very similar. Absorbance techniques are of interest for groundwater measurements, but impractical in soil because the sample is highly scattered.

The state of the art of environmental analysis based upon Laser-Induced Fluorescence (LIF) as a sensing technology is reviewed in this section. The review is limited to:

- the detection and determination of petroleum hydrocarbon components in water and soil matrices using fluorescence spectroscopy,
- in situ measurements using LIF fiber-optic probes, and
- the merger of such technology with the cone penetrometer.

Accordingly, this section outlines the principles of LIF measurements and the key hardware and software options. Fiber-optic LIF technology as applied to the CPT performed by WES within the SCAPS program is reviewed. Alternative excitation, detection, and signal processing schemes and their applicability to the characterization of fuel-contaminated sites found at Air Force bases are presented. Finally, the current version of a laser system designed and built by Dakota Technologies, Inc. for the Air Force is presented.

B. PRINCIPLES OF LASER-INDUCED FLUORESCENCE (LIF)

Fluorescence is the most familiar of several luminescence (light-emission) processes, including phosphorescence, chemiluminescence, bioluminescence, and triboluminescence. Their unifying feature is that photons are emitted as an excited atomic or molecular species drops to a lower energy state. Not all materials are luminescent since there are additional molecular deactivation pathways to light emission. For the present purpose, it is assumed that the fluorescence occurs from molecules that have been electronically excited by light absorption. Fluorescence is distinguished from phosphorescence by the time scale of the emission (fluorescence usually occurs within microseconds or less following the excitation, whereas the phosphorescence emission extends over a longer time period). Fluorescence is distinguishable from other luminescence mechanisms by the means used to create the excitation. In both chemiluminescence and bioluminescence, the molecular excitation is created during reactions that yield high energy. Bioluminescence refers to reactions of a biological nature. Mechanical impact is the source of the excitation in triboluminescence.

Features common to fluorescence experimental apparatuses are:

- a) a light source to induce the photoexcitation process,
- b) optics to deliver excitation light from source to sample,

- c) optics to deliver emitted fluorescence from sample to detector,
- d) detector to convert the light signal into an electrical signal, and
- e) further signal processing.

General comments about each of these features follow.

Light Source - The light source must provide photons of appropriate wavelength to excite the analytes of interest. (Photon energy increases as the wavelength decreases.) For example, the BTEX components of JP-4 jet fuel require excitation photons with wavelengths of about 260 nm to 300 nm. The light source could be a continuous or pulsed laser or an incoherent source such as a mercury or xenon arc lamp. The important design issue is whether the light source can provide the optimal wavelengths of light at a sufficient power density.

Source to sample delivery optics - Remote spectroscopy relies on fiber-optics to deliver the excitation light to the sample. Because fiber-optic diameters are typically less than 1 mm, lasers have substantial advantages over incoherent sources in terms of the optical power density that can be delivered to the sample. Only laser light sources will be considered in the rest of this discussion. The degree to which light is attenuated as it travels along the fiber is a function of wavelength. A variety of fiber types, ranging from plastic-clad to silica-clad, in sizes from 200m to 600 mm have been investigated. In all work, a single source fiber has been utilized.

Sample to detector collection optics - The fluorescence emitted by individual molecules can be considered to take place with an isotropic distribution. With an increasing number and diameter of collection fibers, more light is delivered to the detector (although at additional cost). An alternative to using multiple collection fibers is to use optics to gather the fluorescence from a large area and focus that light onto a single fiber. One of the important trade-offs is fiber cost versus light collection efficiency. The cost of a 50-meter long fiber-optic probe could easily range from as low as \$500 to as much as \$10,000. The lower cost would be represented by a probe with a single collection fiber of relatively small-diameter (approximately 250 micrometer [μm]) plastic-clad silica, whereas the expensive probe would use six collection fibers of large diameter (600 μm) silica-clad silica fiber. Many factors must be considered in the selection of the most cost-effective approach.

Detector - The detector converts the fluorescence photons presented to it into an electrical signal. The usual spectral presentation is a plot of intensity versus emission wavelength. The wavelength resolving device is generally a monochromator, which employs a diffraction grating or

prism to effect a spatial separation of the light. Optical Multichannel Analyzers (OMA) or a Charge-Coupled Device (CCD) are commonly used to record the entire spectrum presented by the monochromator. An alternative arrangement relies on a slit to select a narrow wavelength range of the dispersed emission for conversion to a current or voltage by the photomultiplier tube. This approach can be repeated several times at different wavelengths to generate the full spectrum. The OMA and CCD detectors, make it possible to collect the entire spectrum at once, speeding up the data collection time significantly.

Signal processing - If the excitation source is continuous, the options for signal processing are limited essentially to fluorescence intensity versus wavelength. The lifetime characteristics of the fluorescence can be measured with pulsed excitation. The time period over which the fluorescence is emitted depends on the excitation pulse duration, the chemical identity of the sample, and any temporal distortion introduced by the signal collection and processor instrumentation. Examination of the time profile may provide the basis for improved detection specificity, i.e., the ability to distinguish the chemical identity of the emitting molecules. The combination of a photomultiplier tube with a digital oscilloscope directly provides the emission time profile, although only at a single emission wavelength. To acquire the temporal information with an OMA or CCD detector, the technique of "gating" is required. In gating, the supply voltage to the detector is "on" for only a selected interval and at a selected delay after the photoexcitation. Recording the spectrum as a function of the delay in a discrete series of experiments generates the full-time profile. In either the phototube-digital oscilloscope or gated OMA/CCD approaches, one ultimately can generate a "wavelength-time matrix" (WTM), a multidimensional data presentation with emission wavelength along one axis, fluorescence lifetime along another, and intensity along a third axis.

C. ANALYTICAL SPECTROSCOPY CONSIDERATIONS

There are several reasons why fluorescence is the method of choice for detection of aromatic hydrocarbons by fiber-optic spectroscopy. The range of acceptable light transmission in optical fibers is 200-2500 nm. Spectroscopies that use light in this range include UV-visible absorbance, infrared absorbance, Raman scattering, and fluorescence. Fluorescence has the required characteristics of sensitivity and applicability for hydrocarbons.

Fluorescence is actually the least general of the above techniques. Every organic molecule exhibits transitions between vibrational levels that can be studied by mid-IR and near-IR absorbance and Raman scattering. Electronic absorption (commonly referred to as UV-visible absorption) is associated with transitions between electronic levels. The energy of the absorbed

photon is transferred to a molecule that is raised from its ground electronic state to an excited state. Note that such electronic excitation is also a prerequisite to subsequent fluorescence photon emission. Even though every organic molecule exhibits UV-visible absorbance, it may occur at so short a wavelength as to preclude their study in this fashion. Aliphatic hydrocarbons, which only undergo electronic excitation for photons in the <200 nm range, form such a class.

Chemical analysis by absorption spectroscopy relies on a combination of signal strength and characteristic structure. Because absorbance is so general, samples that contain many different chemical components (including all fuels) will yield spectra that are composites of all their components. Prominent spectral features increase the precision with which component contributions can be extracted by mathematical data processing. UV-visible absorption and fluorescence monitor electronic transitions, which are generally not highly structured under room temperature solution conditions. Chlorinated solvents show weak absorption at wavelengths between 200 and 300 nm, and are poor candidates for direct electronic absorption measurements because they show only edge absorption. In contrast, individual Raman and mid-IR bands, which carry molecular vibration information, may span as little as 0.1% of the usual spectral range and are, therefore, very specific.

Unfortunately, infrared and Raman are not very sensitive techniques. Infrared measurements work well for high concentration samples (neat liquids, dispersions of solids in a nonabsorbing liquid mull, etc.) or gaseous samples, for which the spectral features are extremely narrow.

The major challenge for field application of fiber-optic spectroscopy is speciation capability. Higher spectral dimensionality increases analysis specificity for multicomponent samples. Absorption has a single experimental parameter (wavelength) and is therefore one-dimensional. Fluorescence is two-dimensional if the source is wavelength selectable. Pulsed excitation adds a third dimension, the time scale over which the fluorescence is emitted. Nonresonance Raman scattering is one-dimensional. Resonance Raman scattering is two-dimensional similar to non-time resolved fluorescence.

Fluorescence and Raman are power spectroscopies, i.e., the detected signal intensity is proportional to the excitation flux. They are also ideally zero-background experiments. In reality, there is always some background (from physical scattering or solvent Raman scattering); but fluorescence and Raman spectra usually represent small signals against an even weaker background. High source radiant power is therefore desirable, especially for ultraviolet work since fiber attenuation in this region is large. Background scattering is more of a problem for studies of soils than for groundwater.

UV-visible absorbance generally lacks sufficient sensitivity to be applied to field analysis and its capacity to speciate components is severely limited. There may be some applications to groundwater measurements (Reference 4) but CPT for real-time measurements is not practical because the sample is brought inside the CPT. Infrared absorbance is not applicable to direct aqueous analysis owing to absorbance by the solvent. Moreover, fiber-optics will transmit infrared in only limited spectral regions.

Raman spectroscopy has received considerable attention. Its most attractive feature is the excellent speciation capability due to the sharpness of the spectral features. It resembles infrared in this regard, but benefits because the light is in the visible region where fiber attenuation is low. On the other hand, Raman scattering is usually such an inefficient process that any significant fluorescence, common to the majority of Aromatic Hydrocarbons (AHs), overwhelms the Raman signal. Likely applications of Raman are for process control where concentrations are high enough that sensitivity is no longer an issue.

Two specialized forms of Raman spectroscopy can yield the signal intensities needed to make Raman analysis feasible, despite the background complications. One of these techniques is resonance Raman, a form in which the source wavelength lies in the electronic absorption region of the PAH. For quantum mechanical reasons that have been well documented (Reference 8), the scattering signal is then enhanced by as much as several orders of magnitude. The main reason resonance Raman has not seen greater analytical applications is the requirement for wavelength tunable excitation. Current research indicates that resonance Raman has strong potential (Reference 6, 9,10) but, at this time, a suitable method of calibration is an issue. The Raman signal depends on several parameters including detector angle, collection optics, and many others (Reference 3).

Surface enhanced Raman spectroscopy (SERS) has also received attention as a possible spectroscopic PAH detection technique (Reference 11). SERS exploits the tremendous increase in Raman scattering efficiency which occurs when some organic molecules are adsorbed onto certain metal surfaces. This technique is known to provide excellent sensitivity for some species, especially pyridine, but most PAHs do not appear to exhibit the enhancement necessary for direct analysis at ppb levels. This fact, along with the fragile metal surfaces involved, makes SERS a questionable candidate for field applicability. Much of the current research is focused on the dependence of the enhancement factor on surface morphology.

D. AFSCAPS BACKGROUND

The Tri-Service SCAPS program established by the U.S. Army Corps of Engineers Waterways Experiment Station represents the original combination of fiber-optic measurements and cone penetrometer. As discussed in Reference 1 and summarized in Table 1, the CPT-based environmental characterization system has many advantages over conventional drilling and sampling programs. The original LIF-CPT probe was developed as part of WES's program in this area.

The essence of the WES LIF-CPT idea was to incorporate a sapphire window in the side of the cone, allowing light to be directed from inside the cone onto the soil moving past the sapphire window as the cone is pushed into the ground. The light directed onto the soil is chosen to contain the appropriate wavelength(s) to excite fluorescence of petroleum contaminants on the soil. Fluorescence backscattered into the cone is collected by a fiber-optic cable, which returns the light to the surface for quantification. Originally, WES positioned a mercury lamp downhole in the cone as the excitation source, but soon began to use a laser located in the CPT truck as the source. Light from the laser is directed from the truck into the cone with a second optical fiber. Both the delivery and collection fibers are bundled into the instrumentation cable with the other conventional geotechnical sensors.

E. INFLUENCE OF FUEL TYPE AND SOIL MATRIX

To date, most LIF studies for environmental analysis have mainly dealt with aqueous media (Ref 6). Environmental uncertainties for ground water measurements arise if:

- multicomponent fluorescent compounds exist in solution,
- turbidity (suspended solids content) is high, thereby decreasing the effective excitation energy because of scattering (producing a lower measured intensity), or
- dissolved oxygen levels are variable leading to quenching of the fluorescence.

Corrections for these effects may be made, depending on the development of LIF signal processing and analysis techniques or synergistic sensor technologies.

The Naval Command, Controls & Ocean Surveillance Center (NCCOSC) group (Reference 11), in collaboration with WES, has shown that LIF results for soils are dependent on a larger and more complex set of variables when compared to LIF measurements of aqueous solutions. Generally, the sensitivity appears to depend on soil type (e.g., surface area, grain size,

mineralogy, and degree of soil aggregation), porosity, moisture content, saturation level and LIF response of natural fluorophores (e.g., humic acid). The presence of solids increases the amount of backscattering and decreases the effective penetration depth of the excitation energy. The following paragraphs summarize the main conclusions of the NCCOSC group study.

Table 1 TRI-SERVICE SCAPS STRENGTHS AND LIMITATIONS
U.S. Army Corps of Engineers (Reference 1)

Strengths	Limitations
<ul style="list-style-type: none"> • Screens for chemical contamination characteristics using electrical resistivity and optical properties of soil • Determines soil type from strength data • Includes surface geophysical scanning to detect obstacles/hazards • Allows sealing and grouting of penetrometer holes • Saves time and money over conventional drilling • Minimizes crew exposure to hazardous materials • Allows for decontamination of surfaces and compartments exposed to hazardous wastes • Integrates data into unified databases • Samples soil and groundwater • Collects real-time data and allows partial on-site interpretation • Provides on-site visualization of subsurface conditions • Installs monitoring/sampling devices 	<ul style="list-style-type: none"> • Cannot be used in competent rock or cemented soils without predrilling • Sensors provide only qualitative to semiquantitative measurement of contaminant concentration • Sensors identify classes of compounds only • Soil and water samples are typically smaller than those provided by drilling

For both clay and sand matrices the fluorescence signal is determined only by the contaminant on or between the first grain layer, i.e., the grains in contact with the window. Although they could visually observe fluorescence penetrating slightly deeper into the sample, its contribution to the signal received at the detector is apparently negligible.

The observed fluorescence signal depends on the type of soil matrix. The fluorescence of DFM on Fischer Sea sand increases rapidly with increasing DFM concentration. The signal versus concentration curve has a much lower slope for clay matrices, such as attapulgite and bentonite. For example, at a fixed concentration of 50,000 ppm by weight DFM, the fluorescence signal is an order-of-magnitude greater for sand than for attapulgite clay. The attapulgite signal, in turn, is many times greater than the bentonite signal. Soil type is a factor to be considered when analyzing LIF-CPT signals.

The possibility that the differential fluorescence response could be explained in terms of grain size and/or specific surface area was investigated by the NCCOSC group, but no clear conclusions emerged. Some success was obtained in correlating fluorescence response with an "available" surface area as opposed to the "specific" surface area. The authors concluded that the "fluorescent response of the fluorophore on sands and clays, though affected by several factors, is primarily controlled by the grain surface area available to the contaminant." Unfortunately, there does not appear to be a simple way to determine the "available surface area," apart from very extensive fluorescence calibration measurements.

The influence of water content on the fluorescence signal depends on whether the water is added to the soil matrix before or after the fuel is added. The order effect is small for Fischer Sea sand, but large for illite, a clay material. In fact, the fluorescence of DFM on illite is much higher if water is introduced to the sample and then the DFM is added, as opposed to the addition of DFM first. This is related to the negatively charged surfaces of the clay particles. If the DFM is added first, it is incorporated into the structure of the clay and is not present on the outer "available" surface area. If water is applied first, it occupies the internal structure spaces forcing the DFM to occupy the outer available surface area.

Based upon the above discussions, any methods to correlate LIF intensity to a level of contamination without consideration of the soil matrix effects may lead to erroneous results. Some limited laboratory testing is being conducted by NCCOSC to investigate these effects, but additional work is needed. In the meantime, site-specific correlations can be used with care to produce approximate levels of contamination present.

SECTION III

LIF-CPT SYSTEM SPECIFICATIONS

A. INTRODUCTION

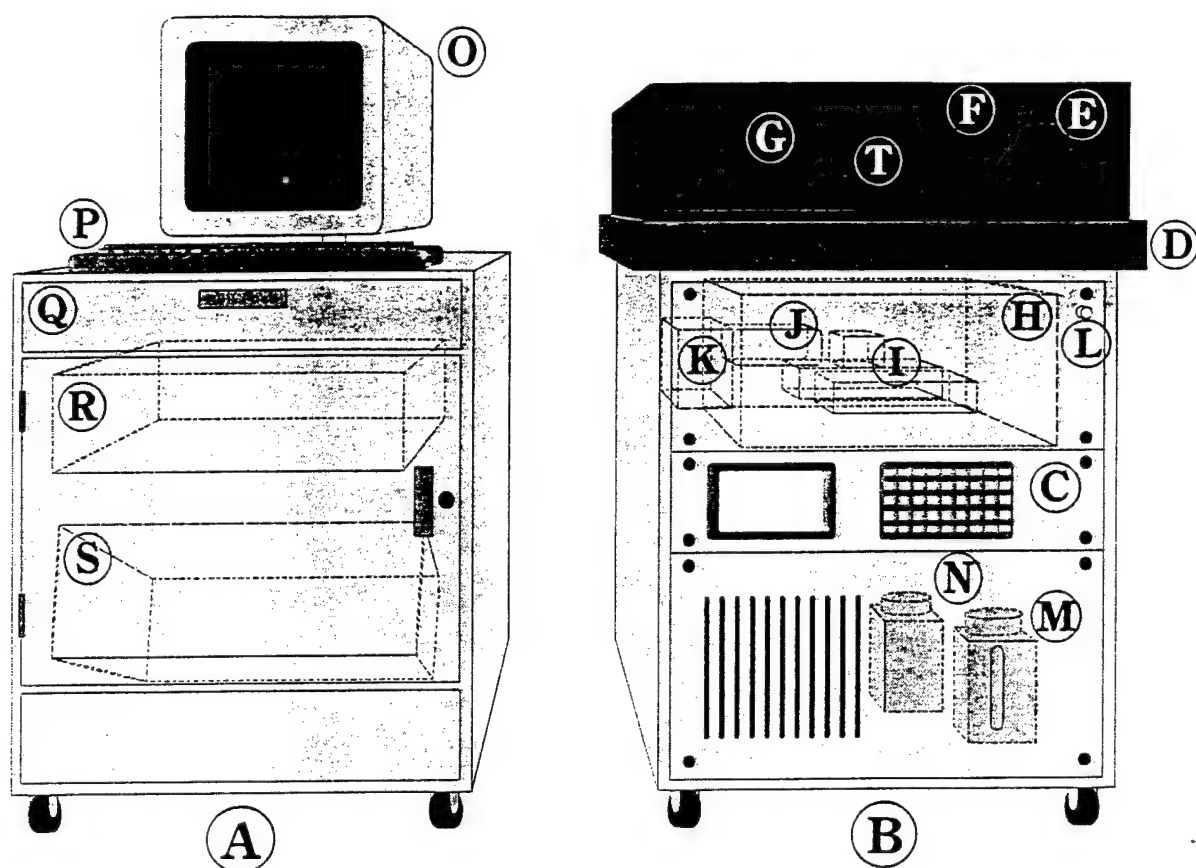
This section presents a discussion of the overall improvements/benefits of the LIF-CPT system developed during this project as compared to the previous system (i.e., the Tinker system), including the laser source, dye lasers, detection scheme, LIF-CPT probe and computer control. Also included in this section is a brief discussion regarding the operation and related safety issues of the LIF-CPT system.

The basic laser system components follow:

- a Nd:YAG pump laser,
- dye laser and amplifier to convert the second harmonic (532 μm) of Nd:YAG to a visible wavelength,
- frequency doubling crystals to convert the visible dye laser output to ultraviolet,
- fiber-optic probe,
- monochromator for wavelength resolution of the return fluorescence,
- photomultiplier tube to convert photons into electrical signal,
- digital oscilloscope for waveform capture,
- and a control computer.

The fiber-optic probe for the cone penetrometer consists of a delivery and collection fiber, protective sheath housing the internal optics, fiber-optic mount within the cone, and sapphire window. The uphole portion of the system is adaptable to either groundwater monitoring fiber-optic probes or an optical cone penetrometer probe.

Figure 1 is a schematic of the main system components: (1) a breadboard with laser and optical mounts and power supply generating signal for the delivery fiber, (2) the fiber-optic probe, and (3) a collection fiber fixed to a monochromator with photomultiplier tube (PMT), digital oscilloscope detection system and control computer (PC).



- | | |
|-------------------------------------|-------------------------------|
| A. Electronics cabinet | K. High-voltage power supply |
| B. Laser cabinet | L. Stepper motor reset button |
| C. Nd:YAG power supply | M. Water reservoir |
| D. Optical breadboard | N. Dye reservoir |
| E. Frequency doubling crystal | O. Monitor |
| F. Nd:YAG laser head | P. Keyboard |
| G. Dye laser | Q. Utility Drawer |
| H. Monochromator | R. Computer |
| I. Stepper motor controller/driver | S. Oscilloscope |
| J. Photomultiplier tube and housing | T. Temperature Controller |

Figure 1. Schematic of LIF System Components.

B. LASER SYSTEM IMPROVEMENTS/BENEFITS

Several significant improvements to the Air Force tunable laser system were developed for this project, and the procedures for conducting LIF-CPT were refined. These improvements are compared to the system used in a previous LIF-CPT project at Tinker AFB. The main features of that system, referred herein as the Tinker system, are briefly reviewed to place the improvements in context. Full details on the Tinker system and field demonstration can be found in the report entitled "Air Force Site Characterization and Analysis Penetrometer System (AFSCAPS); Laser-Induced Fluorescence Cone Penetrometer, Volume I - System Development and Evaluation" (Reference 7).

1. Laser Source

a. Tinker System

The major hardware components of the Tinker system include a Spectra Physics GCR Nd:YAG laser with 2nd, 3rd, and 4th harmonic generator accessory, which pumps two complete tunable dye lasers operating independently of one another. One dye laser operates on Rhodamine 6G dye and is pumped with the Nd:YAG 2nd harmonic (532 nm). The other one operates on Coumarin 500 dye and is pumped with the Nd:YAG 3rd harmonic (355 nm). The output beam of each dye laser is independently frequency-doubled (KDP doubling crystal) to provide tunable, pulsed radiation in the wavelength ranges 282-305 nm and 259-272 nm, respectively. For the Tinker project, the Nd:YAG laser was operated at 10 Hz pulse repetition rate. Operation up to 20 Hz is possible, but output pulse power drops sharply for repetition rates above 10 Hz.

Although the Tinker system performed reliably during the 6-week field test, the system's overall size created crowded conditions in the ARA cone penetrometer truck. The dye lasers, frequency doubling crystals and other launch optics and Nd:YAG pump laser were positioned on a 48-inch x 30-inch x 4-foot optical breadboard. Shock mounts were affixed to the bottom of the breadboard at each corner. For deployment in the cone penetrometer truck, the breadboard was placed on a reinforced plywood board across the countertops and perpendicular to the aisle (approximately 3 feet wide) at the back of the truck. The Nd:YAG laser power supply, which is a cube approximately 2 feet on each side, was positioned in the aisle on the floor beneath the breadboard. The detection system was located on the counter top at the left hand (looking to the rear) side of the truck. The Tinker laser system is too large for air shipment unless the

Nd:YAG laser resonator is removed from the optical breadboard. The system was transported to Tinker AFB from ARA's facility in Vermont in the back of a pick-up truck. Note that the Nd:YAG umbilical cord, (which carries air, water, and electrical power between the power supply and resonator), cannot be disconnected. Loading the system into the cone penetrometer truck required the effort of four people.

The dye laser frequency doubling crystals were not temperature stabilized for the Tinker system, which caused some problems in operation. The doubling crystals must be positioned very precisely for efficient frequency doubling. Both temperature and angle tuning are possible to reach phase matching conditions. If wavelength variation is at all contemplated, then angle tuning is the method of choice as it is much faster; however, temperature variation after the angle is optimized causes reduced doubling efficiency and a significant reduction in power.

Another limitation of the Tinker system was that the Nd:YAG dye laser pump required 208-240 V electrical power. Generators were used to provide this service, but this required additional space on the truck and generated a noise hazard. A better solution would be a laser system that utilizes a 120-volt supply, easily available on the CPT rig.

Probably the biggest problem, however, was a tendency of the fiber-optic probe to undergo pistoning. The softclad "plastic" fiber does not have an actual chemical bond between the fused silica core and the silicone rubber cladding. Under the stresses placed on the fiber during deployment of the cone penetrometer probe into the ground, the core could move in and out of the cladding. Light emerging from the core at the cone end scatters off the cladding "hood," leading to elevated background signals and limits of detection.

b. Current Laser System

The present contract called for a major redesign of the laser system and subsequent testing at several sites where the Air Force and EPA were jointly conducting bioventing and intrinsic remediation studies. After discussions regarding many potential test locations, Plattsburgh AFB, Patrick AFB and Cape Canaveral, and Dover AFB were selected as the three sites for the Phase I studies. There was not enough time between the contract initiation (October 18, 1993) and the scheduled work at Plattsburgh AFB for completion of the redesigned laser system. Therefore, the Plattsburgh work, (performed in late November and early December), actually used an existing laser system temporarily transitioned from Air Force research projects at

North Dakota State University. This system resembled the Tinker system, but the following differences should be noted:

- The breadboard is only 24 inches wide (compared to 30).
- It did not have the second (Coumarin 500) dye laser.
- All components, (with the exception of the monitor of the control computer), are packaged into a single unit approximately 48 inches L x 24 inches W x 36 inches H.
- The digital storage oscilloscope was upgraded to a Tektronix TDS 620.
- The monochromator, (an HR320), has similar optical characteristics as the Spex 270M, but its slit-widths must be set manually.

Several major technical improvements were made to the Air Force Tinker system under the current project:

- The pulse repetition rate was increased from 10 to 50 Hz.
- The Nd:YAG pump laser, including power supply, was downsized from approximately 13 cubic feet volume to 3.25 cubic feet.
- The necessity for 208-240 V power was eliminated; only standard 110 line voltage is now required.
- The digital oscilloscope was upgraded to the TDS 620. The elimination of interleaved sampling at short scope time base settings improves signal to noise ratio.
- The photomultiplier tube of the Tinker system was replaced with a smaller, less costly model.
- The stability of the frequency doubling process was improved substantially by temperature control of the doubling crystal.
- A new shock mounting system was developed to allow transport of the laser system while installed in the cone penetrometer truck.
- More tests and calibration procedures were built into the system. For example, the optimization of the doubling crystal position is now fully automated, which eliminates operator manipulations.
- A 266-nm capability was implemented.
- Improvements were made in the downhole optics. Repairs and alignment can easily be made in the field.

The new system occupies two half-height standard instrumentation racks (19 inches wide, ca. 25 inches high), which can be air-shipped in crates. The air-shipping feasibility was first tested when the system was transported without incident from Fargo, ND, to Lebanon, NH. On a later return of the system to Fargo, one of the crates was completely

destroyed from careless handling by airline personnel. Nonetheless, the laser system's performance was not adversely affected.

A schematic of the two racks is shown in Figure 1. All of the optical instrumentation is located in one rack, and the control computer and digital oscilloscope are located in the other. The new pump laser, which replaces the Spectra-Physics GCR-12, is a Big Sky (Bozeman, MT) CFR-200 unit. The old and new pump lasers are compared in Table 2.

Table 2. COMPARISON OF OLD AND NEW PUMP LASERS.

Attribute	Previous	New
Resonator size	3.5 inches x 1 inch x 1 inch	14 inches x 4 inches x 4 inches
Power supply size	ca. 2 inch cube	2 inch x 2 inch x 4 inches
Pulse repetition	10 Hertz	50 Hertz
Power requirements	1 ϕ , 208-240V,	10 ϕ 110 V
Harmonics	2 nd , 3 rd , 4 th	2 nd (note)

Note: Nd:YAG fundamental (1064 nm) already rejected in Big Sky.

Two key features led to the choice of the Big Sky laser: (1) pulse frequency, and (2) size reduction. In the work at Tinker AFB, either the spatial resolution was compromised to average enough laser shots or the cone penetrometer advancement rate had to be reduced. With the 50 Hz system, we chose to average 50 laser shots, which takes about one second. When the overhead time to download a laser waveform from the digital oscilloscope to the control computer is factored in, a point is acquired about once every inch.

Although the schedule did not permit its testing, a 266-nm capability was also added to the system. Arranging the pump laser head, dye laser cells, frequency doubling crystal, and other optics all on a 24 inches x 24 inches breadboard required careful layout. The optical train of the dye laser began with a 5°, 100% 532 nm reflector. A partial reflector directed 30% of the 532 nm light to the dye laser oscillator. The remaining 70% was turned with another 45°, 100% reflector into the amplifier cell. The cells were the Bethune types described by Bratton et al (Reference 7).

The rhodamine 6G dye laser, when pumped with the Nd:YAG 2nd harmonic, provides visible light in the range 566-610 nm range. Frequency doubling the light in KDP provides tunable UV radiation in the 283-305 nm range. (However, for all of the projects

described in this report, the laser wavelength was held fixed at 290 nm.) This is too long to excite the fluorescence of single-ring aromatic hydrocarbons (BTEX). The Tinker system was designed with a Coumarin 500 dye laser, which when pumped with the Nd:YAG 3rd harmonic (355 nm), provides light that can be doubled to 260-272 nm (a good wavelength range for exciting the fluorescence of BTEX).

The feasibility of the double-dye laser system was proved at Tinker, but could not be retained with the switch to the 50 Hz laser system and the miniaturization. Big Sky does not provide a 3rd harmonic option and no other manufacturer offers a high repetition rate, miniaturized Nd:YAG pump. Current practice indicates that wavelength switching may be required infrequently in the field, in which case a fixed wavelength beam at shorter wavelengths than the Rhodamine 6G laser would suffice. The obvious method was to double the 532 nm 2nd harmonic to 266 nm.

This capability was implemented after considering several options. The easiest optical train would employ a separate doubling crystal for the 532, but this would add considerable expense and complication (an additional rotation stage, doubling crystal, etc.) Additional software would be required. A more elegant approach requiring only one doubling crystal was implemented. The benefits of this approach are the ability to switch on the fly and the capability to run two wavelengths in a single test.

The chosen solution employs beam steering optics on kinematic mounts. To switch to 266 nm operation, the laser is turned off and the cover removed. The optics, (which intercept the 532 nm light before it hits the dye cells), are repositioned, the cover replaced and the laser turned back on. Software automatically switches the wavelength to 266 nm. The doubled light is automatically launched into the same fiber. The rejection filter that blocks scattered laser light from hitting the photomultiplier tube is changed while the laser top is off.

One slight complication that had to be overcome is that the polarization of the Nd:YAG 2nd harmonic is opposite that of the dye laser output, so the polarization of one of the beams must be rotated 90 degrees going into the doubling crystal. In this case, the 532 nm polarization plane rotated with a half-wave plate.

Another important improvement is the ability to monitor and reoptimize the ultraviolet laser power without removing the top. The stability of the dye laser power has also been improved. Previously, the operator had to periodically adjust the position of the doubling

crystal to compensate for temperature changes. By incorporating the crystal in a housing heated 10-15 degrees above the ambient temperature and by adding a temperature control circuit, the frequency doubling stability is greatly enhanced.

The dye laser power can be monitored periodically. A fraction of the ultraviolet beam is launched onto a Molelectron pyroelectric detector. At intervals determined by the operator, the doubling crystal is rocked a few steps on either side of its current position to find if the optimal angle is still valid. This correction is rarely more than a few percent in intensity, but provides another level of quality control.

2. Detection System

a. Photo-multiplier Tube

The detection system developed consisted of a Spex 270M monochromator, Tektronix 2440 digitized oscilloscope, and an EMI high-gain photomultiplier tube. The photomultiplier tube used during the Tinker demonstration and its housing now cost approximately \$2,200, and the housing of the photomultiplier tube is approximately 1 foot long. Converting to the rack design required a smaller photomultiplier tube. The Hamamatsu R-928 was found to be ideal, as it (1) occupies only a few cubic inches, (2) costs about \$800, including housing, and (3) operates at a lower voltage.

b. NOF Detector

The Naturally Occurring Fluorophore (NOF) detector relates to ARA's past experience. ARA's work at Tinker AFB and at the Savannah River Site indicated that many common solvents tend to react with the soils, producing compounds that fluoresce at long wavelengths. This is possibly related to humic substances, (humic and fulvic acid), which are known to be fluorescent. A better understanding of the effect of the NOF's can be obtained by monitoring several wavelengths simultaneously. The NOF detector was developed as an inexpensive method of providing that information.

The basic concept of the NOF detector is that fluorescence can be measured over a broad wavelength region in the visible region, or a total visible fluorescence channel. A simple design was implemented. Light returning from the cone penetrometer probe is split on the optical breadboard into two beams. One beam is piped into the monochromator in the usual

fashion; the other beam is piped to the NOF detector. The detector is a small box that contains an optical filter, photomultiplier tube, and a high voltage power supply to power the PMT. The NOF detector requires standard line voltage input and coax cable carries the signal from the NOF detector to the digital oscilloscope. While the NOF detector was developed as part of this project, it was not field tested.

3. Control Computer

The CS-3 system is controlled by a Gateway 2000[®] 33MHz 486DX computer configured with 8MB of RAM, an internal 250 MB Jumbo[®] tape backup system, a 3.5 inches diskette and a 424MB IDE hard drive. The computer is equipped with a 14-inch non-interlaced monitor (refer to Figure 1, Item O) and a standard AT compatible keyboard (refer to Figure 1, Item P). The computer controls the stepper motor controller and SPEX 270M via RS232 serial communication. Communication with the digital storage oscilloscope is achieved with a National Instruments[®] GPIB interface. A digital I/O board internal to the computer is used as a parallel interface to obtain depth information from the CPT truck. The LIF system is completely controlled via custom software run on the control computer.

The control computer has undergone several configuration changes from the NDSU system used at Tinker AFB. The hard-drive capacity was doubled to increase storage capacity. The internal tape backup system was added to allow for convenient transfer and storage of the large amounts of data generated. The digital I/O board supplied by ARA was a Keithly PIO-96 digital I/O board and was used to communicate between the CPT and laser computer systems. The PIO-96 I/O board provides 96 bits of latched digital input/output. A 32-bit parallel ribbon cable between the I/O cards in the CPT and LIF computer systems was used to transfer depth (1/1000 feet resolution) and LIF waveform area (pico-volt-seconds) between the systems. No computer hardware problems were experienced during the field demonstrations.

4. Data Acquisition and Processing Software

The CS-3 software was written in Microsoft Basic Professional 7.1. The bulk of the code used for this system was written for earlier versions of the instrument at NDSU. The CS-3 Operations Manual (Volume V) contains detailed descriptions of the sequence of instructions used to control the instrument during a CPT-LIF testing. Several major improvements made to the code are documented below.

First, the process of saving the reference and laser waveforms was reduced from a scope/bezel button operation to a menu selection from the main menu. A sequence for background signal acquisition was also added to the main menu. This was added to correct for a DC offset in the fluorescence waveform. This helped to alleviate most the problem, but a random drift in the DC offset made complete correction impossible. The source of this drift was never pinpointed. Another major improvement was the addition of an automatic (hands-off) angle optimization routine for the frequency doubling crystal. This routine was also accessible from the main menu. A joulemeter, positioned to monitor a reflection of the generated tunable UV light, made automation of this process possible. Microprocessor temperature stabilization of the crystal was also added to the instrument to stabilize UV energy levels. This is a stand alone package and was not controlled by the software. Overall, the output power was significantly stabilized over the Tinker system, although some power normalizations are still necessary to develop calibration functions.

C. PROBE DESIGN

1. Introduction

An important finding of the first Air Force Site Characterization and Analysis Penetrometer System (AFSCAPS) project was that the Laser-Induced Fluorescence-Cone Penetrometer (LIF-CPT) probe required improvement (Reference 7). Much of the variability in the performance of the system was caused from the sharp bend radius of the fiber-optic cables inside of the CPT probe. The sharp bend resulted in a high stress concentration that ultimately led to the failure of a glue bond holding the fibers in place. Once this bond failed, the optical fibers shifted in and out (pistoning) of the plastic jacket material. This pistoning caused the plastic jacket material (which fluoresces) to flake off and increased the amount of background noise. A task under the current effort was the development of an improved LIF-CPT optical probe. Specific items to be addressed were an evaluation of plastic clad versus silica clad fibers, alternate fiber-optical cable configurations and inclusion of downhole optics to condition the optical signal. To assist with the design, evaluation and fabrication of the improved LIF-CPT probe, ARA initiated a laboratory study involving Dakota Technologies, Inc. (DTI) and EIC Laboratories. EIC Laboratories were tasked with designing a two-fiber probe using a variety of optical elements. The test program was designed to compare the two-fiber approach with a series of bundled fiber approaches suggested by DTI.

Presented below is a summary of the laboratory test program and analysis of the resulting data. The analysis was used to select the most appropriate probe configuration for field evaluation as a part of the demonstration program. Many of the decisions regarding cable selection

and probe configurations for the test program were made during a meeting at EIC Laboratories on 22 October 1993, between ARA, DTI and EIC. These decisions are summarized below.

2. Cable Evaluation

Both DTI and EIC have experience with a variety of fiber-optic cable configurations. For the original AFSCAPS demonstrations conducted during 1992, a plastic clad 600 micrometers 6-around-1 cable configuration was used. The seven fiber-optic cables were placed in a protective plastic tube, that in turn was placed inside another heavy wall cable along with the CPT probe cable. The heavy wall plastic tubing was required to protect the fiber-optic cable from excessive tube bending. The heavy wall plastic tubing could not be bent into as sharp a radius as the fiber-optics. This configuration worked; however, it proved to be operationally difficult. Therefore, a cable configuration was selected that would provide protection and flexibility to the fiber-optic cables without using excessively large and heavy plastic tubing or conduit.

During the October 22, 1993 meeting, it was jointly decided to switch from plastic-clad to silica-clad fiber-optic cables. The plastic-clad fibers were used on the first AFSCAP project because of their low cost compared to silica clad fibers. Also the transmission characteristics of plastic-clad fibers were not as good as those clad in silica. The plastic-clad fibers proved to be unsuitable for use in the CPT in a 6-around-1 configuration because of the separation of the plastic cladding from the silica fiber at the probe, as discussed above. Therefore, the design was switched to silica-clad, offering better optical performance and eliminating the pistoning problem. The major question then became the selection of optical fiber diameters for transmission and collection of the laser light and fluorescence.

For the excitation fiber, DTI had previously used 600- and 400-micrometer fiber for laser light excitation. Their experience was that the pulsed laser light is so strong that fiber damage occurs when smaller fibers are used. EIC has successfully used 200 micrometers fibers for this type of work, although they have not used exactly the same laser as DTI. A compromise of a 400-micrometer fiber for excitation was reached. For the collection fibers, DTI had experience using 600-micrometer fibers on the previous LIF project and with the water well probes previously developed. EIC proposed using 200-micrometer fibers, since these are more economical, and, when combined with downhole focusing optics, should provide adequate signals.

During the October 1993 meeting, discussions revealed concerns regarding attenuation through the fibers and transmission characteristics of the downhole optics. Both DTI and EIC indicated that models to evaluate the light transmission for various optical configurations

of sufficient accuracy were not readily available. Even if the models were developed, a laboratory study would still be required to verify the model calculations. Based on this inability to accurately model the various fiber-optic configurations, a laboratory test program was conducted and is presented in the following subsection.

3. Laboratory Test Program

Under the laboratory testing program, five different probe designs were evaluated. Key evaluation criteria were background levels and maximum signal (light) delivered to the uphole spectrometer. The primary variables in the testing program were evaluations of multi-bundle light collections versus a single fiber light collecting system. The benefits and possible drawbacks of focused light as opposed to unfocused light were also reviewed. In addition to technical evaluations of the laboratory test results, other criteria included in the final evaluation of the probe systems were reliability, repairability, ease of use, and system cost.

a. Probe and Test Configuration

A total of five probe configurations were evaluated in eight experimental setups. In general, each probe was evaluated in one setup, with the exception of the plain bundle probe which was tested both normal and 30° to the sample. Configurations tested in the laboratory are shown in Figure 2. Both the Configuration E (reflected, collimated and focused, bundled) and Configuration F (EIC) probes were tested with 5 mm and 7.5 mm focal lengths.

For all experiments, measurements were made on two samples. One sample was 1000 ppm of JP4 on silica sand and the second sample consisted of clean silica sand. Each sample was contained behind a 2 mm thick, antireflection coated sapphire window and rotated at a rate simulating the CPT as it penetrated through the ground. In addition to simulating actual conditions, rotating the sample averaged out local sample hot spots, producing more uniform measurements. For each experimental setup, the probe to sample distance was varied from as close to the sample as possible to approximately 8 mm from the window face, in steps of 1 or 2 mm. This assisted the selection of optimal stand-off distances between the probe and the sample. For each of the measurement distances, the laser was pulsed 20 times, and 8 sets of the pulses were averaged to determine the value for the measurement. Exactly the same measurement sets were performed for both clean and contaminated samples.

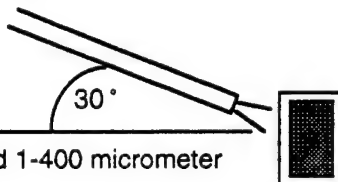
Experiment A

8-200 micrometer around 1-400 micron

Clean Sand or Sand with
1000 ppm Gasoline by Weight

Rotating Sample
Holder with a
Sapphire
Sample

Experiment B



8-200 micrometer around 1-400 micrometer

Experiment C

8-200 micrometer around 1-400 micrometer



Experiment D

6-200 micrometer around 1-400 micrometer

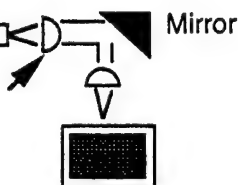
Collimating and Focusing Lens



Experiment E1 and E2 (see Tables)

6-200 micrometer around 1-400 micrometer

Collimating and Focusing Lens



Experiment F1 and F2 (see Tables)

400 micrometer collection fiber

400 micrometer excitation

Collimating Lens

Collimating and Focusing Lens

340 nm
Dichroic
filter

Mirror

Mirror

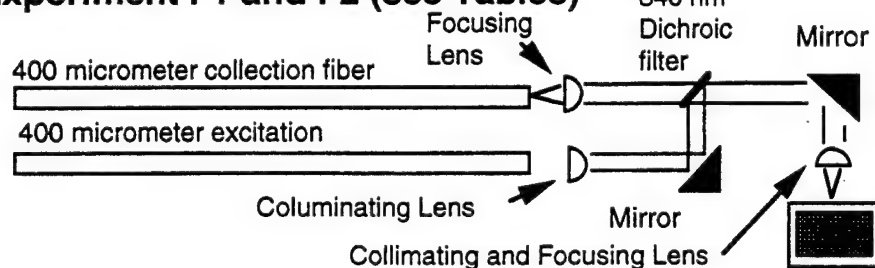


Figure 2 Schematic of LIF-Probe Testing Configurations.

In configurations A through D, the probe used 8-200 micrometer collection fibers around 1-400 micrometer transmission fiber. The number of collection fibers was increased from the previous 6 to 8 to account for the reduced fiber cross section created in going from a 600 to 200 micrometer fiber. The increase also maximized the number of fibers that could surround the transmission fiber. Configuration A served as the baseline experiment to which all other configurations were compared. This configuration was basically the same as the original AFSCAPS demonstration (Reference 7). In experiment B, the same configuration was used, except that the optical fiber bundle was inclined 30° to the sample. In experiment C, the same 8-around-1 fiber system was used, except it was reflected 90° off a mirror onto the sample. The return light traveled back off the mirror into the 8 collection fibers. Experiment D consisted of the same setup as experiment C, except the excitation reflected signals were collimated, with the reflected signal focused onto the fiber bundle. The signal was reflected back off the mirror and focused onto the fiber bundle. For the final 8-around-1 experiment (E1 and E2) a lens was added to focus the excitation laser light onto the sample and collect the back scatter signal.

The second major probe configuration was similar to the EIC Raman probe design in that a single transmission fiber and a single collection fiber were used. Downhole optics were used to direct the light and filter out background light induced in the optical fiber as the light is transmitted from the laser to the probe. This system involves the use of a dichroic filter to reflect a narrow band of excitation light to the sample while transmitting only longer wavelengths of collected light to the collection train. Two experiments (F1 and F2) were conducted with this configuration using a sample lens focal length of 5 mm and 7.5 mm, respectively.

All experiments were conducted on both clean and contaminated samples, and recorded for a 290 nm excitation wavelength with a collection wavelength of 340 nm. All experiments were conducted at North Dakota State University (NDSU) chemical laboratory using 10 meterlong silica fiber sections of the required diameters. As discussed previously, experiments were conducted where distance between the probe and sample were varied from as close as possible to longer distances determined to be reasonable for the cone penetrometer. Power at the sample was measured for each configuration. A summary of test results from each of the experiments is contained in Table 3, which presents: (1) average signal intensity obtained from the JP-4 sample, (2) average signal intensity obtained from a clean sand sample, and (3) signal-to-sand background ratio for each configuration. All reported distances are from the sample. Finally, the column labeled "Resolution" was calculated by multiplying the calibration factor (1000 ppm/max signal) by the clean sand intensity value, which is the limiting background noise.

Table 3 LIF-PROBE TEST RESULTS

Experiment Probe	File Name Sample	File name Sand	Distance to Sample mm	Signal Intensity (LIF)	Sand Intensity (LIF)	Signal/ Background	Resolution ppm
A Bundle Straight On	A-22	A-28	2	42644	638	66.84	14.96
	A-23	A-29	4	40472	552	73.32	13.64
	A-24	A-30	6	31034	392	79.17	12.63
	A-25	A-31	8	23788	187	127.21	7.86
	A-26	A-27	4	38161	457	83.50	11.98
B Bundle 30°							
C Reflected	B-05	B-09*	2	1450	5	290.00	3.45
	B-06	B-10*	4	795	5	159.00	6.29
	B-07	B-11*	6	880	2	440.00	2.27
	B-08	B-12*	8	666	-1.5	-444.00	-2.25
D Collimated Reflected	C-06	C-10	2	2848	73	39.01	25.63
	C-07	C-11	4	2428	67	36.24	27.59
	C-08	C-12	6	1958	64	30.59	32.69
	C-09	C-13	8	1748	68	25.71	38.90
E1 5mm Collimated Focused Reflected	D-25	D-30	2	6294	109	57.74	17.32
	D-26	D-31	3	7037	115	61.19	16.34
	D-27	D-32	4	6654	104	63.98	15.63
	D-28	D-33	5	5289	83	63.72	15.69
E2 7.5mm Collimated Focused Reflected	D-29		6	4117			
	D-41	D-34	2	3195	143	22.34	44.76
	D-42	D-35	3	2903	137	21.19	47.19
	D-43	D-36	4	3144	141	22.30	44.85
F1 5mm EIC Probe	D-44	D-37	5	3738	146	25.60	39.06
	D-45	D-38	6	3938	144	27.35	36.57
	D-46	D-39	7	3716	137	27.12	36.87
	D-47	D-40	8	3169	132	24.01	41.65
F2 7.5mm EIC Probe	E-01	E-06	2	2709	17.4	155.69	6.42
	E-02	E-07	3	4862	33	147.33	6.79
	E-03	E-08	4	5751	39.9	144.14	6.94
	E-04	E-09	5	3489	26	134.19	7.45
F2 7.5mm EIC Probe	E-05	E-10	6	1857	11.6	160.09	6.25
	E-11	E-19	2	1445	3.1	466.13	2.15
	E-12	E-20	3	2146	9	238.44	4.19
	E-13	E-21	4	3122	16	195.13	5.12
F2 7.5mm EIC Probe	E-14	E-22	5	4201	23	182.65	5.47
	E-15	E-23	6	4227	31.16	135.65	7.37
	E-16	E-24	7	3018	30	100.60	9.94
	E-17	E-25	8	1936	22	88.00	11.36
	E-18	E-26	9	1309	9.5	137.79	7.26

Notes: * sand measurements are suspect due to large shift in laser power.

b. Correction for Power Losses

For the experiments in which the mirror was used to turn the laser light by 90 degrees, a correction was made to the power transmission. The mirror was inadvertently coated with silver, which improves the power transmission for visible to near infra-red wavelengths. However, in the 266- to 340- nm range of interest, the coating attenuates the power transmission by about 20% for 340 nm, 86% for 290, and 96% for 266 nm. (The 266 and 290 nm attenuation factors were measured and 340 nm estimated from the data and manufacturer's specification data sheets.) Because of this, only the bundled probe configuration delivered significantly more laser power to the sample than the other configurations using mirrors to turn the light beam. With the proper mirrors, the mirrored probe systems deliver roughly 95% of the laser light to the sample. For actual probes, the power delivered would be approximately the same for all probe configurations when appropriate mirrors are used. To correct for the inefficiency of the mirrors, the average signal intensity has been corrected for the excitation power loss through the mirror as:

$$I_{\text{calc}} = \frac{P_{\text{baseline}}}{P_{\text{probe}}} * I_{\text{probe}}$$

where:

I_{calc} = Calculated LIF Intensity

P_{baseline} = Measured power of the Baseline Probe

P_{probe} = Power measured at the probe (mv)

I_{probe} = Measured intensity of LIF signal

The LIF intensity data in Table 3 have not been corrected, whereas the LIF intensity data in Table 4 have been corrected using Equation (1) for each mirrored probe configuration. For the fluorescence signal generated by the sample and reflected by the mirror back into the collection fibers, the additional loss occurs at the 340 nm wavelength. It is estimated (based on the manufacturer's specification) that the mirror returned only 80% of the fluorescence light to the fiber-optics. As it was not possible to measure the actual reflectivity at 340 nm, no correction was made for this loss. Since no correction was possible, the maximum signal intensity used in this evaluation is believed to be a lower limit for those experiments that used a reflecting mirror.

c. Fluorescence Intensity

Several conclusions were made regarding the test data in Tables 3 and 4. In general, for diverging configurations such as Experiments A and B, maximum intensity was obtained for those experiments with the probe closest to the sample. The intensity of Experiment C was quite poor because the total distance from the excitation fiber to the sample was quite long (see Figure 2). Experiment D shows that collimation of the light beam significantly increases both the signal intensity and S/B ratio. The signal for experiment D was still weak because the excitation beam area (i.e. power density) was relatively large. Again, moving away from the sample decreased intensity, (presumably caused by imperfect collimation), but the effect was much less pronounced.

Unlike the other bundle configurations, Experiment E probe mockups produced maximum intensities at longer distances near their respective lens focal lengths (where the smallest laser spot sizes are achieved). As expected, the shorter focal length lens performed best and gave the overall highest normalized intensity of any configuration.

Like the focused bundle configurations, the "EIC" configuration in Experiments F1 and F2 also gave maximum intensity near the design focal length, with the 5 mm lens outperforming the 7.5 mm lens. The normalized intensity with the 5 mm lens was the second best overall.

d. Signal to Background Performance

Reevaluating the results from the perspective of signal-to-background ratios (S/B), the F series configuration was best, probably due in some measure to its laser rejection in the fluorescence collection train (see Table 4). For all the configurations using focusing optics, the maximum S/B ratio occurred near but not directly at the focal point, where background scatter from the sand was also highest. For the bundle only configuration (A), S/B increased in the opposite direction of maximum intensity because the background dropped off with distance faster than the fluorescence signal. With increasing distance, the S/B improved, peaking at 8 mm from the sample (the maximum distance tested). Eventually, at large distances, the background signal strength dropped into the noise and the advantage of this approach was lost. A distance of about 8 mm is probably near the longest practical working limit inside the cone penetrometer. At 6 mm a S/B of 80 is achieved (about half that of the F configuration).

Table 4 SUMMARY OF "BEST" LIF-PROBE CONFIGURATION TEST DATA

Configuration	Maximize Signal				Minimize Noise			
	Max Signal LJF	Dist. (mm)	S/B Ratio	Resolution ppm	Max S/B Ratio	Dist. (mm)	Signal LJF	Resolution ppm
A Bundle Probe Normal to Window	42644	2	67	15	127	8	23788	8
B Bundle Probe 30 deg to Window	38161	2.5	83.5	12	83.5	2.5	38161	12
C Bundled Probe Reflected*	17220	2	50	20	50	6	10450	20
D Bundled Probe Reflected & Collimated	24613	2	39	26	39	2	24613	26
E1 Bundled Probe Reflected, Collimated, & Focused (5mm)	66851	3	61	16	64	4	63213	16
E2 Bundled Probe Reflected, Collimated, & Focused (7.5mm)	37411	6	27	37	27.3	6	37411	37
F1 EIC 2 Fiber Probe (5mm)	49668	4	144	7	155.7	2	23396	6
F2 EIC 2 Fiber Probe (7.5mm)	36505	6	135.6	7	195	4	26962	5

* S/B ratios are estimated due to power shift prior to sand measurements

Table 5 LIF PROBE RANKING RESULTS, BASED ON MINIMUM NOISE DISTANCE

Configuration Based on Min. Noise Probe	S/B Ratio	Signal at Min Noise	Cost	Reliability	Repairability	Ease of Use	Tunability	Total Score
Weights Factor->	10	8	4	8	8	8	4	50
A Bundle Probe Normal to Window (baseline)	100%	100%	100%	100%	100%	100%	100%	50
B Bundle Probe 30 deg to Window	66%	160%	100%	100%	100%	100%	100%	51
C Bundled Probe Reflected	39%	44%	80%	100%	80%	100%	100%	37
D Bundled Probe Reflected & Collimated	31%	103%	75%	100%	80%	100%	100%	41
E1 Bundled Probe Reflected, Collimated, & Focused (5mm)	50%	266%	50%	100%	80%	100%	80%	54
E2 Bundled Probe Reflected, Collimated, & Focused (7.5mm)	21%	157%	50%	100%	80%	100%	80%	42
F1 EIC 2 Fiber Probe (5mm)	123%	98%	75%	200%	200%	200%	60%	74
F2 EIC 2 Fiber Probe (7.5mm)	154%	113%	75%	200%	200%	200%	60%	78

Limited data were obtained at the secondary 266 nm wavelength. Trends similar to those at 290 nm would be expected. The lower background, with the excitation wavelength further from the fluorescence measurement wavelength, improved S/B ratios for the baseline configuration. The mirrored configurations were not tested because the reflectivity was measured to be about 4% at 266 nm.

4. Other Evaluation Criteria

In addition to the technical evaluation criteria, we evaluated cost, reliability, repairability, ease of use and tunability (see Table 5) since these affect system usage costs. The maximum signal and optimum signal to noise ratio evaluation of all probe configurations were compared to the standard 8-around-1 bundled probed configuration. Some of the evaluations are based on ARA's experience with the original AFSCAPS demonstration and a demonstration program for the Department of Energy using the EIC Raman probe and cable configuration. A discussion of the evaluation factors is presented below. To compare the overall performance of the various probe configurations, a matrix was developed in which the various factors were given numerical ratings and weighting factors. These rating factors and the total score for each probe configuration are summarized in Table 5.

a. Signal to Background Ratio

The signal-to-background ratio of a probe was given the highest weighting factor, as this ratio determines the system resolution. To date, the limiting factor to LIF systems has been resolution, not power. A system which delivers more power to the soil sample with a corresponding increase in background has not changed the resolution limits. Based on this criteria the configuration F probe with a 7.5 mm focal length has the highest rating in Table 4. The probe distances which minimize the S/B ratio were used to rank the various configurations. The rankings were obtained by dividing the S/B ratio by the S/B ratio of the bundled probe normal to the window (configuration A). This result is presented as a percent in Table 5.

b. Maximum Signal

Maximum signal at the detector was rated as being the second most important factor in comparing the various LIF probes. While good resolution is most important, it is also important that the system deliver adequate signal to the detector so that noise induced by the

measuring system is minimized. Configuration E had the highest rating; however, its signal-to-noise ratio was quite poor.

c. Probe Cost

Cost of the LIF probes was weighted relatively low in this analysis, as the probe cost is low compared to the cost of a CPT truck equipped with an LIF system and the operations cost. The probes_ costs were estimated, as presented in Table 6 and based on fiber cost provided by manufacturers. Component costs to construct LIF probes with downhole optics are based on estimates provided by EIC and ARA and presented in Table 7. In addition to the initial probe cost, we have included replacement/repair costs for broken cables, including CPT truck down time to repair or replace the cable. We have estimated repair or replacement of one cable per year primarily caused by a CPT rod break, which would result in the fiber-optic cables being cut. The cable for the bundled option is assumed to be lost, as we normally break CPT rods only when a significant length of rods is in the ground. For the 2-cable fiber-optic probes, a field kit is available for repair.

d. Reliability

Reliability of the system was given a high weighting factor, as it affects the production rate and ultimate cost effectiveness of the LIF-CPT probe system. The EIC probe system was rated as being more reliable than the bundled approach, primarily because of the reduced number of fibers. The probability that one of the fibers in the bundled approach will break is four times greater than that of the two-fiber approach since there are twice as many fibers. If a collection fiber breaks on the bundled approach, the remaining fibers can be used; however, this will reduce the signal level returned to the detectors. The reliability of all probes was rated as being equal, assuming that the bonding and pistoning problem of multiple fibers can be solved by the use of silica clad fibers.

e. Repairability

Repair of the system was also given a high weighting factor, as our experience with a variety of CPT probes has shown. Systems break under field conditions and easy repair increases the CPT truck productivity. With this in mind, we rated the EIC probe as more easily repaired based on actual field experience. As part of the Raman-CPT project, we broke a CPT probe and severed a cable when threading on a push rod. Replacing the CPT probe and inserting the Raman module

**Table 6 COMPARISON OF LIF-CPT ESTIMATED PROBE COSTS
(ALL PROBES PROTECTED)**

Configuration (all based on 50 meter probe)	50 meter Probe	Replacement or Repair Cable Cost	Down Time Cost at \$300.00/hr	Total
A	\$ 4125.00	\$ 3625.00	\$ 1200.00	\$8,950
B	\$ 4125.00	\$ 3625.00	\$ 1200.00	\$8,950
C	\$ 4625.00	\$ 3625.00	\$ 1200.00	\$9,450
D	\$ 5125.00	\$ 3625.00	\$ 1200.00	\$9,950
E1 and E2	\$ 5625.00	\$ 3625.00	\$ 1200.00	\$10,450
F1 and F2	\$ 6500.00	\$ 100.00	\$ 300.00	\$6,900

Table 7 SUMMARY OF LIF PROBE COST COMPONENTS.

Component	Estimated Cost
Bundled Version	
8 around 1 Cable	\$ 72.50/m
Bundled Probe	\$ 500.00 each
Mirror	\$ 500.00 each
Collimation Lens	\$ 500.00 each
Focusing Lens	\$ 500.00 each
EIC Version	
Two fiber Cable	\$ 50.00/m
Probe	\$ 4000.00 each

inside the new probe was relatively easy because of the optical connector incorporated into the Raman probe. Repair of a bundled probe involves either cutting off the bundles and polishing and re-gluing inside the probe, or re-stringing the optical cable through the entire rod string, which takes 4 hours.

f. Ease of Use

Ease of use was also given a relatively high rating. This judgment was based primarily on cable handling, as the probes themselves are all equally easy to use. Based on our experience with the AFSCAPS and Raman projects, the two fiber options have been

significantly easier to use. For this option, the optical fibers are treated essentially as another electrical cable, as they have the same degree of protection and flexibility. For the bundled option, the protective jackets become quite thick and less flexible. This increases the difficulty of threading the optical cables through the CPT rod string as well as the push rod handling.

g. Tunability

Tunability was judged in regards to changes required to the probe if the laser excitation wavelength was changed. It was given a relatively low weighting factor as: (1) the 290 nm laser wavelength has been the dominant wavelength used to date, and appears to be more than adequate for the detection of JP-4 (which is the Air Force's primary contaminant of concern); and (2) if the contaminant is known, (i.e. JP-4 on the flight line versus gasoline at the base service station), the laser excitation wavelength can be selected at the beginning of the investigation. For the bundled approaches using no downhole filtering or focusing, no change to the probe system is required. For the systems with downhole filters and focusing lenses, the optical probe must be changed. In the case of the bundled approach, this means changing the cable and probe as the pair function as a single unit. With the EIC approach, this involves changing the optical probe, which is readily removed and disconnected from the transmission and collection fibers.

5. Conclusions

Based on the normalized maximum intensities, the results indicate that a focused configuration produces the strongest fluorescence. The highest fluorescence was given with the use of a 5 mm focusing lens in either the Experiment F configuration or "collimated/reflected/focused" configuration (Experiment E). Based on S/B ratios, the configuration F performed best, followed by the Experiment A configuration at long distances from the sample.

The final column in Table 5 is the total rating of the probes. This rating is the sum of the individual ratings multiplied by the weighting factor. The ratings indicate that bundle versions A, B and E1 are all near equal, with versions C and E2 rated well below the baseline concept. The EIC concept for either the 5 mm or 7.5 mm focal length were rated well above the bundled concept. The technical criteria (S/B max signal) are equal or better than the bundled concept. Major advantages of this system are in regards to field use and long term cost. The total rating is well above that of the bundled approach and is the approach that was carried forward for AFSCAPS demonstrations.

D. OPERATION OF THE LIF-CPT SYSTEM

The LIF system is controlled by an independent computer and connected to the standard ARA CPT computer via a digital I/O board. Following a thirty minute warm-up period for both the computers and laser systems, the test is initiated by calibrating both the LIF and CPT. The LIF is calibrated by holding a standard solution of 2.5 percent JP-4 jet fuel in hexane up to the window and setting the LIF response to 4,095. The CPT tip, sleeve and pore pressure instruments are calibrated according to standard operating procedures presented in Volume II, Section II. Based on the laboratory studies and past experience, the tunable dye laser was set to produce 290 nm excitation during the push, and the emission monochromator was normally set at 340 nm.

Once the probe is calibrated, it is lowered to the ground surface. The probe is pushed into the ground at a constant rate by two hydraulic push cylinders. Measurements of tip stress, sleeve stress and pore pressure are made at an interval of one sample every second, whereas the LIF data are acquired at one sample every 4 seconds. The LIF data measured during the pushing phase is the area under the time decay curve of the fluorescence response at an emission wavelength of 340 nm [3 seconds data transfer]. The data is continually acquired whenever the probe is moving.

A fluorescence "count" is defined as the area under the fluorescence waveform that is equal to 1 bit (1/4095) of the area under a standard waveform of 2.5 percent JP-4 jet fuel in hexane measured prior to testing. In other words, a fluorescence count of 2,047 would indicate that the integrated contaminant waveform would have one-half the total fluorescence area under the waveform (the integrated waveform) as the standard produced. While this "count" system does not consider the background signal and rise time information, it does serve as an excellent "coarse" indicator of contaminant fluorescence, and thus, concentration.

The LIF-CPT system takes advantage of both "active" and "static" modes provided by cone penetrometer testing. Using a constant excitation wavelength, the push mode enables spectral or time-resolved LIF data to be collected at regular depth intervals along with the CPT data (tip stress, sleeve stress and pore pressure). The Tinker laser spectrometer was set up to provide time-resolved fluorescence waveforms at 340 nm during the push. Since fluorescence is a stochastic process, multiple laser shots were averaged to improve the definition of the LIF waveform. It was determined that averaging 16 waveforms was adequate for the LIF-CPT. About 4 seconds were required to average the waveforms and download the data to computer memory. The LIF data were downloaded to two file types: normalized intensity (counts) that was transferred to the CPT

control computer, and the actual waveform data that were stored on the LIF control computer hard disk. The fluorescence waveform data could be used for further analyses, such as lifetime or intensity measurements.

When areas of significant concentration were encountered, the LIF system operator signaled to the CPT operator to pause the sounding. At this point, the technician acquires a WTM (Wave Time Matrix) that contains both time and wavelength information about the contaminant fluorescence. The same excitation wavelength used in the push mode was used in generating the WTM (290 nm). Each WTM consisted of 20 waveforms collected at 10 nm intervals between 300 nm and 500 nm emission. Two-hundred and fifty-six traces were averaged to produce each waveform. Using these settings, the WTM measurement took approximately 5 minutes.

SECTION IV

SUMMARY OF FIELD DEMONSTRATIONS

A. INTRODUCTION

ARA and Dakota Technologies, Inc. (DTI), in cooperation with Engineering-Science, Inc. (E-S), the US EPA Robert S. Kerr Environmental Research Laboratory (RSKERL), conducted Demonstration, Testing, and Evaluation (DT&E) of the LIF-CPT system at Plattsburgh AFB, Patrick_AFB/Cape Canaveral Space Center, and Dover AFB. The following is a summary of the objectives and activities at each of the DT&Es.

The field demonstration and evaluation program had two major objectives. The first was a demonstration of a CPT-deployed, tunable-wavelength LIF system that could be used to locate fuel-contaminated soils. Work by Gillispie (6) has demonstrated that the lower bound LIF detection limit for aqueous solutions is on the order of 100 ppb for toluene in an aqueous solution. Detection limits in soils are significantly higher because of the increased complexities, such as variability in soil type, soil grain size effects, humic acids and the influence of time on the fuel degradation. The first-generation AFSCAPS system was able to obtain a detection limit of 100 ppm total volatile hydrocarbons (TPH) in soils (Reference 7). Demonstrations conducted under the effort evaluated the improved system in three different geologies.

The second major objective of the DT&E program was to collect data required to assess the potential of each site for use as a natural attenuation remediation experiment. To accomplish this objective, a significant portion of the demonstrations centered around the installation of miniature monitoring wells and the collection of water samples. These water samples were used to collect measurements for pH, dissolved oxygen (DO), carbon dioxide (CO₂), as well as other chemical parameters. Because these testing methods are more sensitive than the LIF, the investigations emphasized areas with lower contaminant concentrations (i.e., the outer perimeter of the plume). For this reason, the data analysis for evaluation of the LIF system is rather limited, consisting of a few points where concentrations were high enough for detection by the LIF system.

During the Plattsburgh demonstration and while the new system was being built, the Tinker laser system was used. The new system was completed and used during both the Patrick AFB and Dover AFB demonstrations. For a detailed discussion of the general techniques used for CPT testing and/or an in-depth discussion of the activities conducted at each of the DT&E's the reader is referred to Volumes II, III, and IV of this report.

B. FIELD ACTIVITIES

1. Plattsburgh AFB

The first DT&E was completed at Plattsburgh AFB, located in northeastern New York. The purpose of this DT&E was to define the down-gradient edge of the oily phase petroleum hydrocarbon plume proximate to the FT-002 fire training area (Figure B-1-1) and to provide necessary data to support Bioplume II® modeling efforts by others. The DT&E was conducted from November 30, 1993, to December 10, 1993, and was coordinated with data collection initiatives by both the United States Environmental Protection Agency (US EPA) and Engineering-Science, Inc.

During the 2-week demonstration, a total of 73 CPT pushes at 31 locations were completed. At many of the locations multiple pushes were conducted to obtain water and soil samples. In addition to standard cone penetration, several technologies were demonstrated including Laser-induced Fluorescence (LIF) profiling, soil gas surveying, resistivity profiling, groundwater and soil sampling, and the installation of small-diameter monitoring wells.

Review of available data suggests that the eastern (downgradient) edge of the oily-phase plume was adequately defined during the course of this investigation. The toe extends approximately 620 feet east-southeast of the source (FT-002 fire training pits) as shown in Figure 3.

Soils encountered during this investigation consisted primarily of medium to fine, poorly graded sands with little or no fines, with the exception of an occasional seam of silty fine sand. Granules were predominantly sub-angular to subrounded. These soils are classified as 'SP' according to the Unified Soils Classification System (USCS).

2. Patrick AFB / Cape Canaveral AFB

An intensive subsurface investigation of soil and groundwater was conducted for the ST-29 site located at Patrick Air Force Base (AFB), Florida. Additional field studies were performed at the former fire training area at Kennedy Space Center, Cape Canaveral, Florida. These investigations commenced 21 March 1994 and were completed on 01 April 1994. The three objectives of these investigation were to:

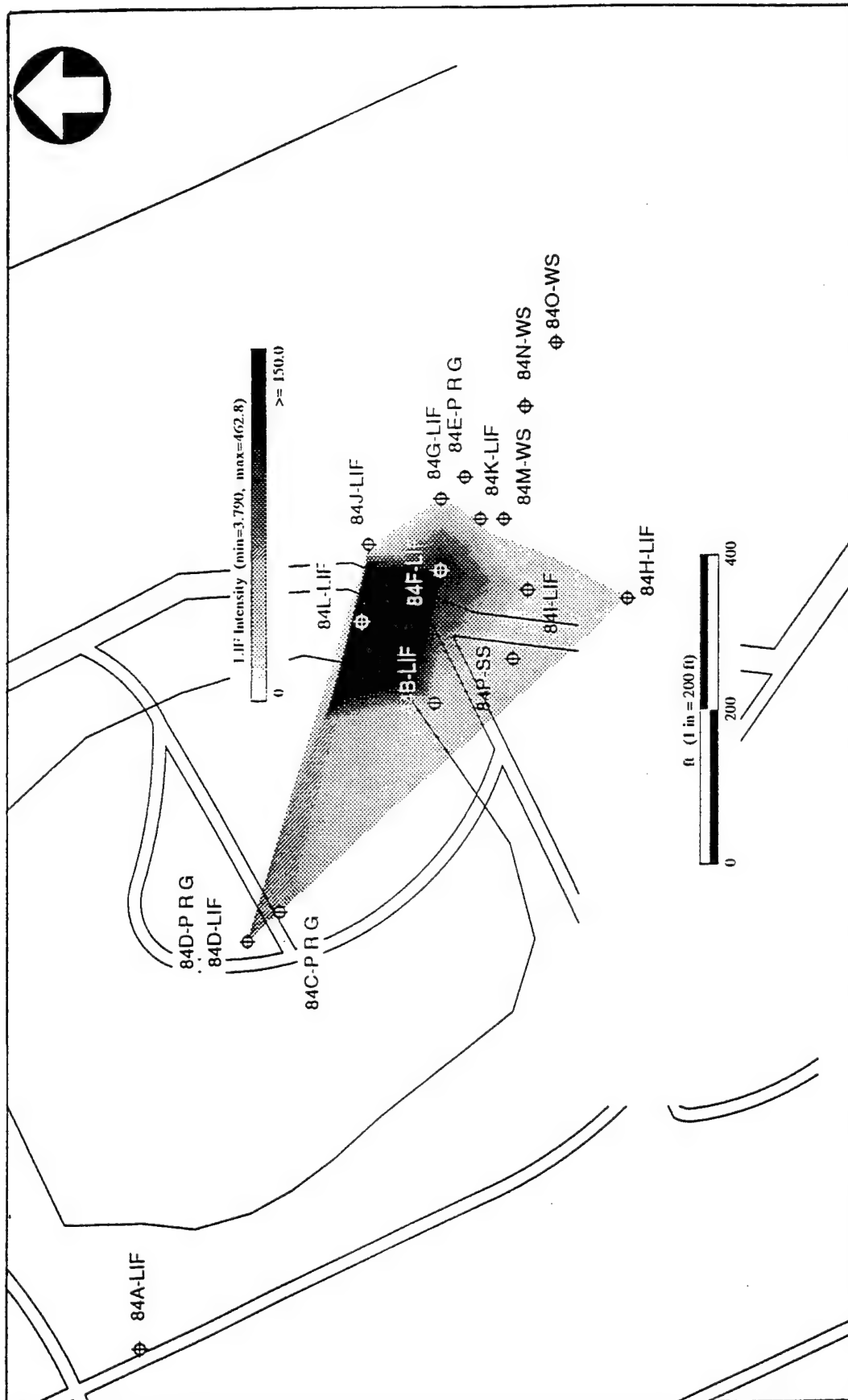


Figure 3. The Downgradient Extent of the Oily Phase Plume at FT-002 Site Plattsburgh AFB, NY.

- Demonstrate the CPT's capabilities to quickly locate and define the areal and vertical extent of the liquid-phase plume using LIF, and to rapidly install monitoring points and collect soil samples to provide additional data necessary to define the dissolved-phase plume, and
- Adequately assess the subsurface conditions at the ST29 site to allow E-S to model the potential for natural attenuation using the Bio-Plume II numerical model,
- Provide data collection capabilities to support the US EPA's efforts aimed at modeling the fate and transport of chlorinated solvents at the former fire training area noted above.

During the Patrick AFB investigation, ARA completed a total of 18 LIF-CPT soundings. Figure 4 depicts the locations of these soundings. Based upon these data, 40 successful 0.5-inch monitoring wells were installed to various depths to allow collection of groundwater samples for subsequent chemical analyses. In addition, 19 soil samples were obtained to provide additional data required for the Bioplume II® modeling and to allow correlation with both the CPT and LIF profiles.

A total of 11 LIF-CPT soundings were completed at the former fire training area located at the Kennedy Space Center, Cape Canaveral. Interpretation of these data allowed effective placement of 11 monitoring wells and collection of eight soil samples. Inspection of the CPT profiles indicates that the overburden soils at the ST-29 site consist of various gradations of sands with occasional discontinuous seams of silty clays and clay. This interpretation is in agreement with findings from previous investigations (Reference 12). A summary of soundings completed and respective well completion details and soil sampling intervals at this site are included in the respective section of Volume III.

3. Dover AFB

ARA and DTI, in cooperation with Engineering-Science, Inc. (E-S) and the 436 SPTG/CEV office at Dover Air Force Base, jointly conducted an intensive subsurface investigation of soil and groundwater at the SS27/XYZ and D-7 sites located at Dover Air Force Base (AFB), Dover, Delaware. This investigation commenced 11 April 1994 and was completed on 21 April 1994. The dual objectives of this investigation were to:

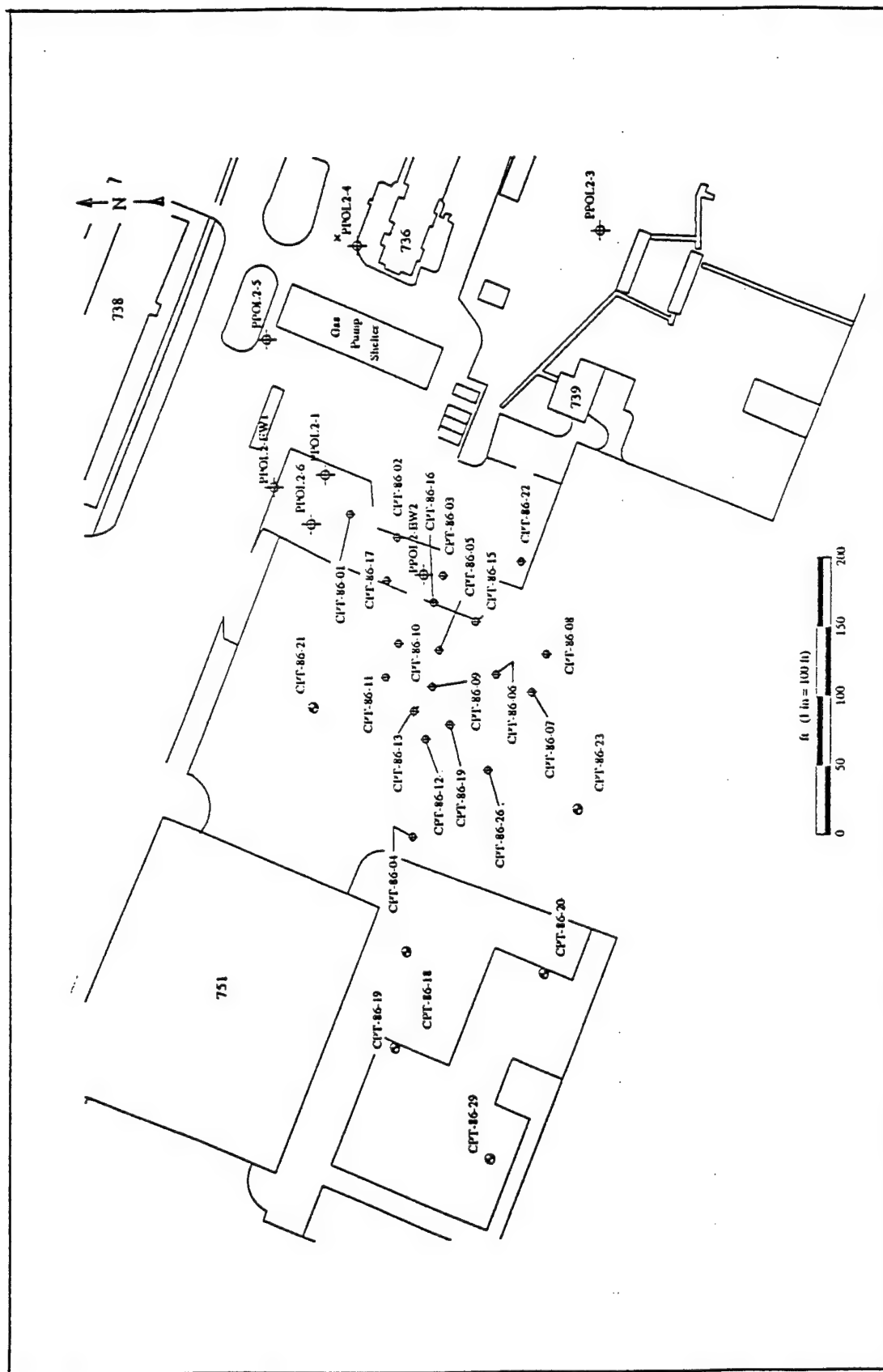


Figure 4. Locations of LIF-CPT Soundings Conducted at the ST-29 Site, Patrick AFB, Florida.

- adequately assess the subsurface conditions to allow E-S to model the potential for natural attenuation using the Bio-Plume II numerical model, and
- demonstrate the CPT's capabilities to quickly locate and define the areal and vertical extent of the liquid-phase plume using LIF, and to rapidly install monitoring points and collect soil samples to provide additional data necessary to define the dissolved-phase plume.

During the course of this investigation, ARA completed a total of 29 CPT soundings, 26 that included LIF analysis. Figure 5 depicts the locations of these soundings. Based upon these data, 33 successful monitoring wells were installed to various depths to allow collection of groundwater samples for subsequent chemical analyses. In addition, ten soil samples were obtained to provide additional data required for the Bioplume II® modeling and to allow correlation with both the CPT and LIF profiles. A summary of soundings completed and respective well completion details and soil sampling intervals is included in Volume IV.

The LIF-CPT proved to be a useful and efficient tool for conducting a subsurface site investigation at the SS27/ XYZ site located at Dover AFB, in Dover, Delaware. The CPT data accurately described the lithology of the site as interbedded clays, silts, sands, and gravels as well as mixtures thereof. This interpretation closely matches interpretations described by others during previous investigations. The CPT data was used to effectively set monitoring wells and collect soil samples. The LIF data assisted in defining both the horizontal and vertical extent of the liquid phase plume.

During the ten-day CPT program, several advantages of the AFSCAPS system were demonstrated:

1. The CPT is minimally invasive and generates no drilling waste.
2. The CPT is a rapid test and greatly reduces cost.
3. Continuous profiling of soil stratigraphy and contamination can be made in which even the thinnest soil layers can be detected. For many sites, thin sand seams carry the majority of the contaminants and are difficult to locate with conventional drilling techniques.
4. Real-time determination of soil stratigraphy, water table depth and degree of contamination can be made with the LIF-CPT. These data are used to optimize the location of the next sounding. On full-scale investigations, this capability can greatly reduce the time required to characterize a site, and result in a more thorough

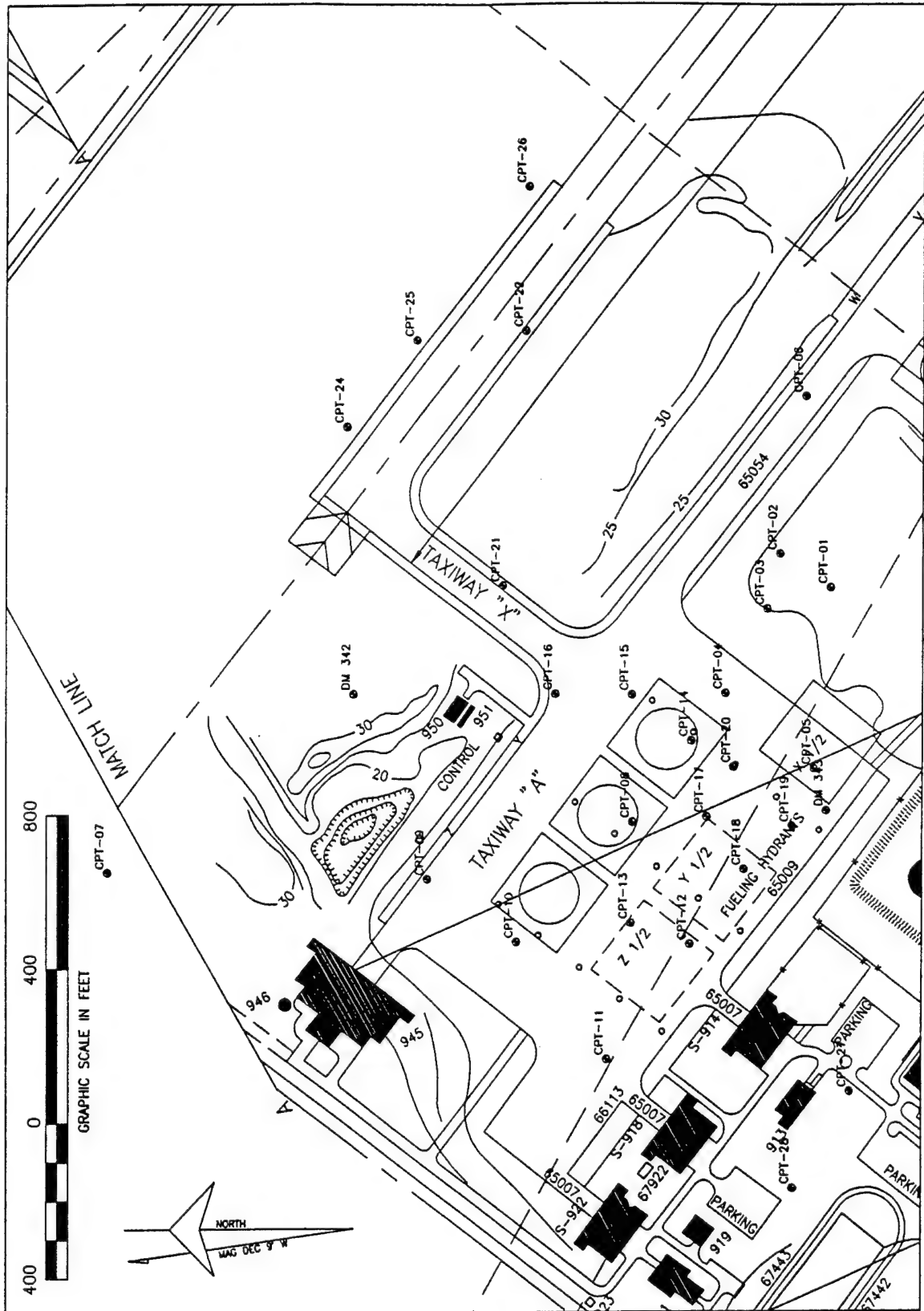


Figure 5. Locations of LIF-CPT Soundings Conducted at the SS27/XYZ Site, Dover AFB, Delaware.

investigation and a greater understanding of the spatial distribution of the contaminant than possible with conventional drilling and sampling methods.

SECTION V

LIF DATA ANALYSIS/EVALUATION

A. RELIABILITY, STABILITY AND REPEATABILITY

Reliability, stability and repeatability under field conditions are primary concerns in evaluating any new instrumentation system. While formal evaluations of the second generation LIF-CPT system have yet to be made, some qualitative and quantitative evaluations can be made by comparing field results from the demonstrations at Patrick AFB/Cape Canaveral, and Dover AFB with the analytical results from the sampling activities. This analysis will provide insight into the parameters that seem to influence the LIF data and how significant they may be. Sections B through D compare LIF data from both clean and contaminated locations to the corresponding chemical data to determine what correlations between the two exist.

B. LIF-CPT SYSTEM BACKGROUND LEVELS

One of the major objectives of the project was to determine if the LIF-CPT probe could be used to detect in situ petroleum oils and lubricants (POL) contamination. The ability to use laser-induced fluorescence techniques as an indicator of the presence of hydrocarbon contamination was demonstrated during the field investigation at Tinker AFB using a first generation Nd:Yag laser system. The previous LIF system's sensitivity to soil type and chemical concentration was of primary concern and left several unanswered questions. To evaluate the new LIF system and gather a better understanding of the minimum contamination detectable, a limited data set of only high quality data from the Dover Site was analyzed. This site was selected because the LIF system was fully optimized and the chemical data was more extensive.

The first step in the system evaluation was a review of the system background response in uncontaminated soils, as this factor effects the lower detection limits. Plots of LIF-CPT profiles from two relatively clean locations are shown in Figures 6 and 7. The CPT data at XYZ-CPT-02-LIF indicates a sequence of fine grained soils near surface, graduating to coarser grained sands below the water table (located at a depth of 7.18 feet). The LIF data indicate a background response of about 50 counts from the surface to a depth of 10 feet, which then decreases to nearly zero below 10 feet. There was only one groundwater sample analyzed at this location, as shown in Figure 6, and that analysis indicated a total BTEX concentration of 3.5 ppb. Assuming that the concentration at this location is well below the detection limit and no response is generated, the LIF profile indicates that the background signal is only very slightly effected by variations in soil type.

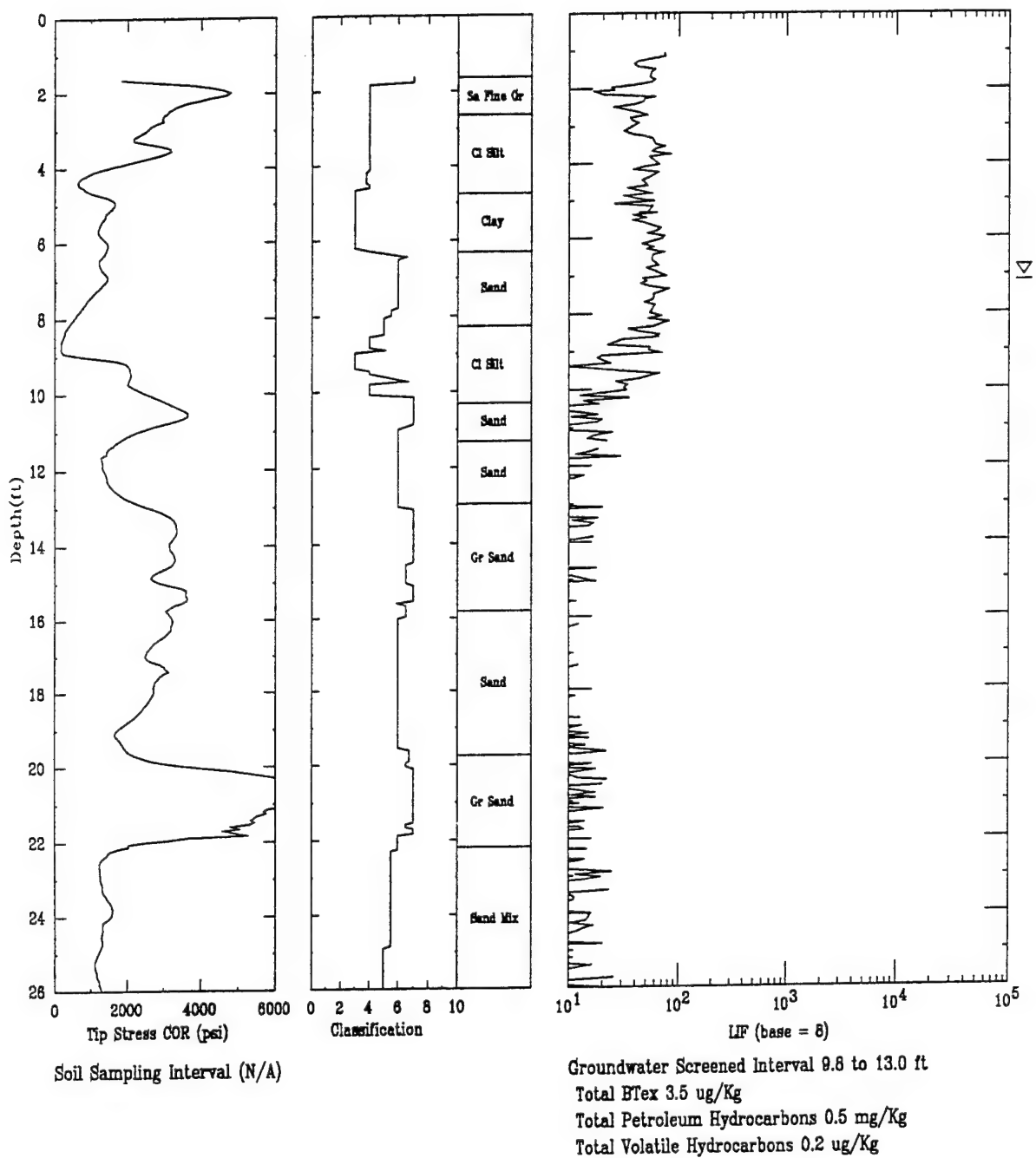


Figure 6. LIF-CPT - 02 in a Clean Area Showing System Background Limits.

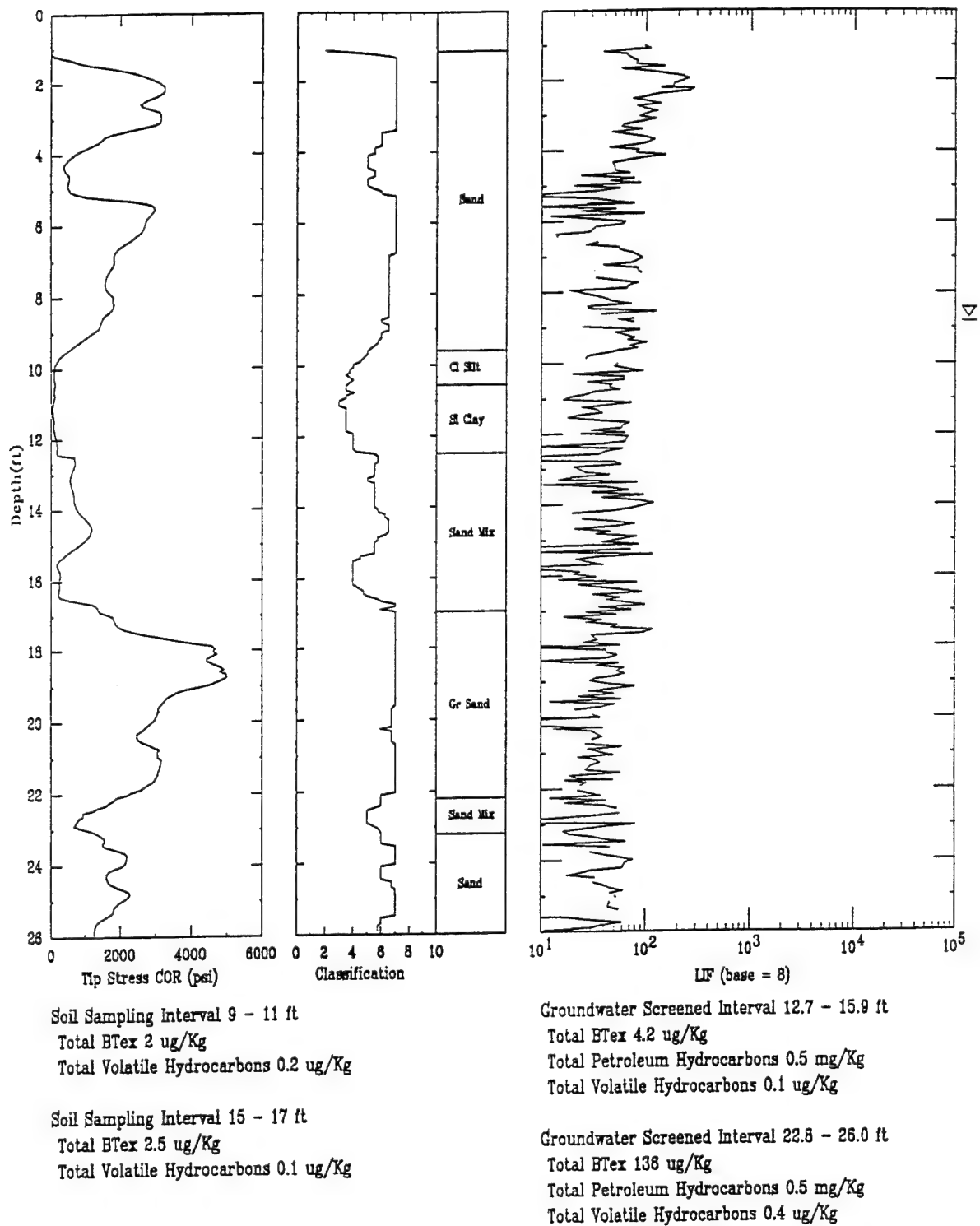


Figure 7. LIF-CPT Profile at a Slightly Contaminated Site Showing Background LIF Lower Limit.

The decrease in the LIF baseline (from 50 counts in the upper 10 feet of the profile to nearly zero) appears to be due to the soil type, as the upper 10 feet is predominately fine grained soils, whereas the lower materials are coarse grained sands.

A plot of the LIF-CPT data from location XYZ-CPT-19-LIF is given in Figure 7. This location is also relatively clean within the shallow zone. The chemical data indicate a total BTEX concentration of 2 ppb in the soil sample interval from 9 to 11 feet, and 4.2 ppb in the groundwater. Total petroleum hydrocarbon (TPH) concentration of 0.5 ppm was also measured in the groundwater. Once again, these contaminant levels are below the demonstrated detection limit of the LIF-CPT probe and no detectable response to the contamination is expected. This location is predominately coarse grained, with a silty clay layer just below the water table of 9 feet. The LIF baseline decreases from a high of 200 counts near the surface to roughly 50 counts below a depth of 4 feet. The soil materials are fairly constant between 1 and 3 feet, and again between 5 and 9 feet. The soils between 1 and 3 feet are most likely fairly dry, whereas the soils below the clayey silt are directly above the water table and nearly saturated. The change in the LIF response is likely due to the moisture content difference as has been noted by Lieberman (Reference 13) in his laboratory studies.

The data from these two profiles seem to indicate that the background limit of LIF-CPT probe is fairly independent of soil type but may have a weak dependency on moisture content, as the average counts in these relatively clean areas appear to decrease slightly in zones of higher moisture content. Based on the data presented and the analysis of data from other profiles from relatively clean areas, the background response of the LIF-CPT probe as configured is roughly 50 counts. Any data obtained below this value must be interpreted as below the system detection capabilities.

C. INFLUENCE OF SOIL TYPE AND CONTAMINANT ON LIF-CPT

The next analysis conducted was to evaluate the influence of soil type on the LIF signal in the presence of a high degree of contamination. Comparisons between analytical tests on soil samples and the LIF-CPT data are made at locations 14 and 16 from the Dover site, as these locations exhibit a high degree of contamination. Comparisons to water sample data are also made at locations 15 and 18 as these locations also indicate a high degree of contamination. Comparisons of these highly contaminated areas will serve to highlight any geologic influences on the LIF data.

At location XYZ-CPT-14-LIF (see Figure 8) the CPT data indicate a coarse grained sandy soil to a depth of 8 feet. From 8 feet to 13.5 feet, fine grained soils are encountered and below 13.5 feet coarse grained sands are again encountered. The water table depth at this location is estimated to be 14.2 feet, hence the LIF data in the upper portion of the profile would not be influenced by the groundwater.

The LIF profile at Location XYZ-CPT-14-LIF indicates a high degree of contamination (average counts >10,000) between depths of 3.4 feet to 8.5 feet and 13.7 feet to 17 feet. A reduced contamination zone (average counts of approximately 2,000) is present from 8.5 to 11 feet, with background levels from 0 to 3.5 feet, 11 to 13.5 feet, and below 17 feet. A soil sample was obtained at the water table interface from a depth of 13 to 15 feet. The total BTEX concentration was 5,255 ppb and the total volatile hydrocarbon concentration was 1100 ppb for this sample. No soil samples were analyzed for TPH at any of the Dover CPT locations. The primary concern with the LIF data at this location is that it is reduced and of very low intensity in the fine grained soil layer from 8.5 to 13.5 feet. A visual description of the soils from 13 feet to 13.6 feet indicates a very stiff clay with a strong hydrocarbon odor. From 13.6 feet to 15 feet, the soil was described as a saturated coarse grained sand, with a strong hydrocarbon odor. The log of the soil sample and CPT soil classification are in good agreement. Apparently the fine grained soils between 8.5 feet to 13.5 feet are contaminated with fuel, yet from 8.5 to 11 feet the LIF response indicates a reduced level of contamination, then drops to background levels between 11 and 13.5 feet. Since both the gravelly sand regions show the same LIF intensity, it is reasonable to postulate that the same level of contamination is present in all materials between these two regions. If the contamination is consistent, then the LIF response should also be consistent. Since the LIF response is significantly reduced in the fine grained layer and the contaminant level is constant, (i.e. high concentrations were detected by both odor and sight from core samples), it appears that the soil type is influencing the LIF response. The reduced response for a high level of contamination indicates that the sensitivity of the LIF system is reduced in this soil type. Previous research by both ARA and others have indicated that the sensitivity of the LIF system is reduced in fine grained soils as compared to sands.

The LIF-CPT data at location XYZ-CPT-16-LIF is plotted in Figure 9. The data are similar to the previous location, in that a silty clay seam at a depth of 8.1 feet to 10.1 feet lies between an upper gravelly sand layer and a lower sand material. The LIF data indicates a highly contaminated layer from a depth of about 5 feet to 8.5, which agrees with the soil chemical analytical data.

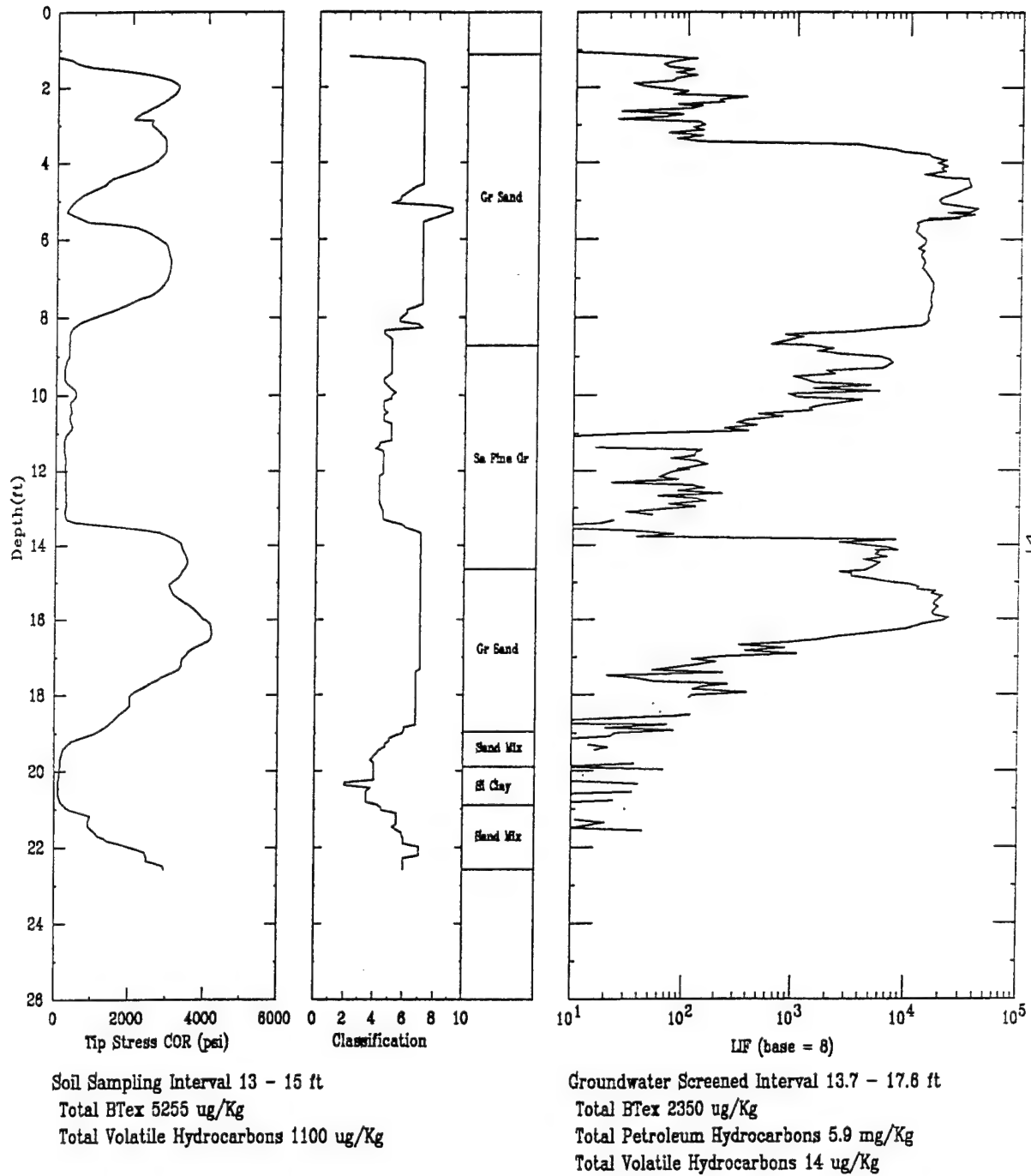


Figure 8. Comparison of LIF-CPT-14 to Soil Analytical Data. Note Low LIF Counts in "SA Fine Gr" Soils.

The analytical data are based upon a soil sample obtained from 7 to 9 feet and indicate a total BTEX concentration of 111,800 ppb and a total volatile hydrocarbon (TVH) concentration of 360 ppb. Based on this large of a sample interval, the top half of the clay layer is contaminated, although a much smaller sampling interval would be required to confirm this contamination. It is likely that the sample was homogenized in the collection procedure, destroying the level of detail required. At the silty clay layer immediately below the upper gravelly sand, the LIF decreases sharply, which may be due either to a decrease in the degree of contamination or a decrease in the sensitivity of the LIF due to soil type effects. The analytical data at a depth of 11 feet to 13 feet indicate a decrease in the contaminant level beneath the clayey layer which should be expected. Insufficient analytical data are available to confirm if this clay layer is serving as a barrier to the spread of the contaminant.

The ground water data at this location tends to indicate that the LIF is not sensitive to the level of contamination (i.e., the dissolved phase) observed in groundwater wells. The contamination level varies from 157 ppb of total BTEX at the 10.2 feet to 13.4 feet depth to 480 ppb of total BTEX at the 20.9 to 24.1 feet depth, while the LIF response remains at a background response level of 50 counts. Both of the contamination levels are above state and federal regulatory limits.

A comparison of the LIF-CPT data to chemical analysis of groundwater samples is given in Figures 10 and 11 for the groundwater samples with the highest degree of contamination. The LIF-CPT profile in Figure 10 is for location XYZ-CPT-15-LIF at Dover AFB and shows a high degree of contamination from the bottom of the pavement (at a depth of 1 foot) to a depth of 14 feet which is in the center of a silty clay layer. The interpretation of the data is that the silty clay layer is limiting the spread of the contamination. It is interesting that at this location, a high LIF count is observed in the silty clay layer, unlike other locations. The water sample from a screened interval of 14.7 to 17.9 feet indicates a high degree of contamination (BTEX concentration = 11,270 ppb). From 15 to 15.9 feet the LIF indicates mild contamination (~100 counts) that decrease to background levels with depth. As these are sandy soils, the LIF signal should be strong. Our interpretation is that the LIF data reflects discrete soil contamination, which is decreasing with depth over this interval. We believe the water sample is a reflection of the average degree of contamination and does not accurately reflect the degree of contamination through the entire sample interval. Also, the level of contamination is only slightly above the system capabilities.

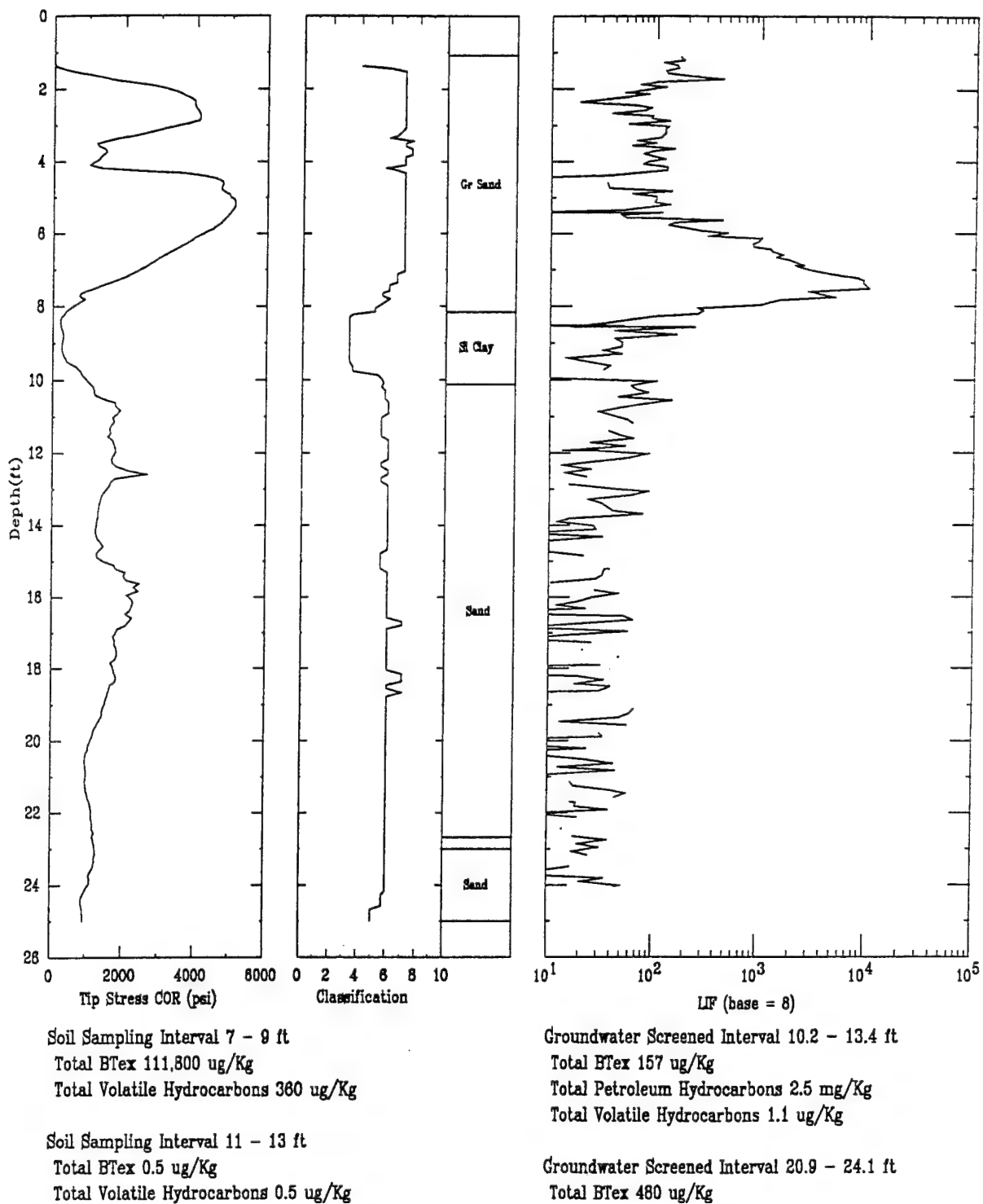


Figure 9. Comparison of LIF-CPT-16 to Soil and Groundwater Chemical Analytical Data. Note Decrease in LIF Count at Silty-Clay Layer.

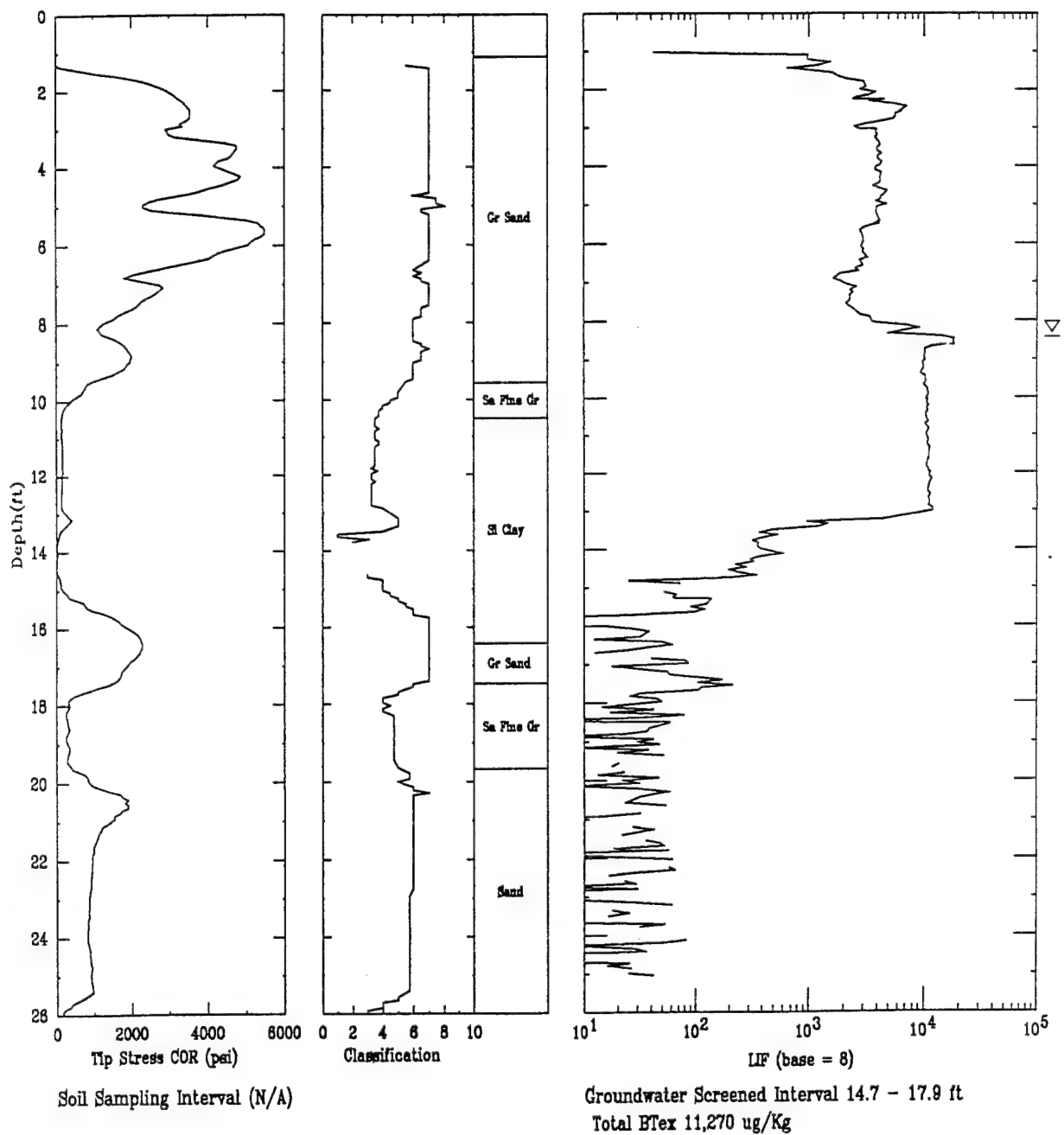


Figure 10. Comparison of LIF Results from LIF-CPT-15 to Chemical Analytical Results of Groundwater Samples from the Same Location. Note LIF Observed in Silty-Clay Layer.

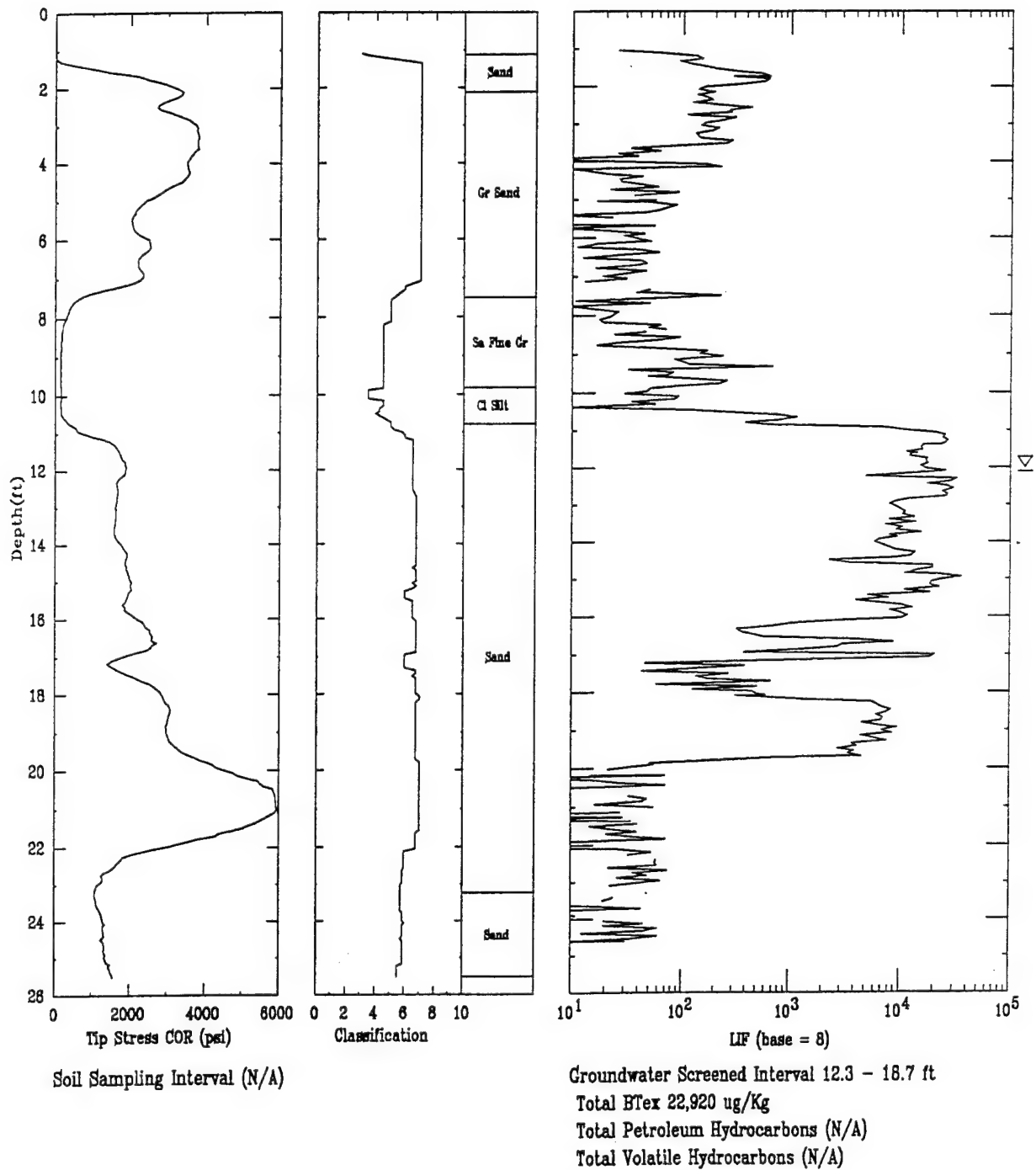


Figure 11. Comparison of LIF Results from LIF-CPT-18 to Chemical Analytical Results of Groundwater Samples from the Same Location. Note LIF Below the Water Table.

At Location XYZ-CPT-18-LIF, the fluorescence response indicates minor contamination near the surface, with a large degree of contamination being located beneath a clay-silt layer at a depth of 9.8 to 10.8 feet. A groundwater sample from a screened well between 12.3 and 18.7 feet produced a total BTEX concentration of 22,920 ppb, confirming the LIF response.

Based upon the above discussion, there are concerns regarding the response of the LIF system in different soils. At some locations the LIF response indicates contamination in clayey layers, yet at others, where inspection of soil samples indicate fuel contamination, the LIF does not produce any response. Examination of the available chemical data is inconclusive, as the data set is very sparse. The groundwater sample data represent an average sample over a several-foot screen interval, whereas the LIF system gives a very detailed response with depth. Other sampling intervals and types give better comparisons, but some locations still exist where the analytical data indicate contamination and the LIF response indicates no contamination. At all locations, the proper chemical data for comparisons to the LIF data have not been obtained. The LIF response was keyed upon naphthalene as the marker compound in the fuel contamination, but chemical analysis response for naphthalene was not performed. In the future, additional chemical data should be obtained to correlate with the LIF data. However, for the primary purpose of this investigation (i.e. natural attenuation studies), this type of data is not required and therefore was not obtained by the primary researcher. It is unfortunate that this type of data is unavailable to complete evaluation of the LIF system.

D. CORRELATION OF AVAILABLE CHEMICAL DATA TO THE LIF DATA

The second aspect of the analysis was to determine if a correlation existed between the LIF and analytical data. Comparisons were made between the analytical data and the average LIF counts measured over the length of the sample interval. Comparisons of the TPH and TVH data are given in Figures 12 and 13 for the Dover AFB sites. TPH and TVH analysis was not performed on the samples from other sites. The amount of analytical data is sparse and no correlation could be developed.

Next a comparison was made of the LIF and BTEX compounds for each of the three demonstration sites. This data were also too sparse to develop site specific correlations, although, if combined, sufficient data appeared to exist for development of a correlation. To determine if a correlation could be developed a rank analysis of the data was performed.

A rank analysis consists of independently ranking two parameters in order of magnitude to determine if a correlation exists. This type of analysis is particularly useful for data which spans

several orders of magnitude or for highly non-linear data sets where simple examination of the data may not reveal a relationship. A rank analysis also assists in the reduction of data scatter. In a rank analysis, the dependent and independent variables with the highest values rank the highest (i.e., have the highest rank value). A perfect correlation would lie on a line with a 1 to 1 slope.

The rank analysis of the total BTEX and total xylene data obtained from soil samples from all three sites is plotted in Figure 14 and 15, respectively. As can be seen in both figures, the rank analysis indicates that a correlation does exist between the total BTEX and total xylene concentration and the LIF responses. The BTEX data shows more scatter in the rank analysis, as expected, because the lighter BTEX compounds are more volatile (see Table xx) and degrade more readily than the heavier compounds. The xylene data scatter fairly tightly around the 1:1 slope, indicating that a good fit to the data should be expected.

The total BTEX and total xylene concentrations versus the LIF counts for soil samples only, at all sites, are plotted in Figures 16 and 17. The data are plotted as log-log, as both the analytical and LIF data spans several orders of magnitude. Least squares fits have been applied to the data as shown. The r^2 of the fits are .9118 and .9181 respectively, indicating a fairly strong correlation. The correlations can be used to estimate the total BTEX and total xylene concentrations at these sites; however, the correlations must be used with caution for two reasons.

The first reason is that the LIF system deployed at the sites used an excitation wavelength of 290 nm, which is not sufficiently low to excite the BTEX compounds. In addition, the emission wavelength monitored during the push was 340 nm, which is significantly longer than the emission peak of the BTEX compounds (Reference 14). The relationships plotted in Figures 15 and 16 show a functional relationship between total BTEX and total xylene concentrations that is not related to the physical properties being measured. The LIF system is measuring the fluorescence of compounds that have peak emission spectra around 340 nm, such as naphthalene. Most likely, the BTEX and xylene compounds not being excited by the 290 nm light have a similar response to naphthalene-like compounds, which are excited. The fits plotted in Figures 16 and 17 can be used to estimate the total BTEX and total xylene concentrations; however, great care should be used and analytical samples collected to confirm the estimates.

The second area of concern is that the a first-order linear relation is expected between fuel concentration and LIF intensity. Laboratory study has shown this type of response is based on fitting the peak excitation wavelength for a given contaminant. The second order fits in Figures 16

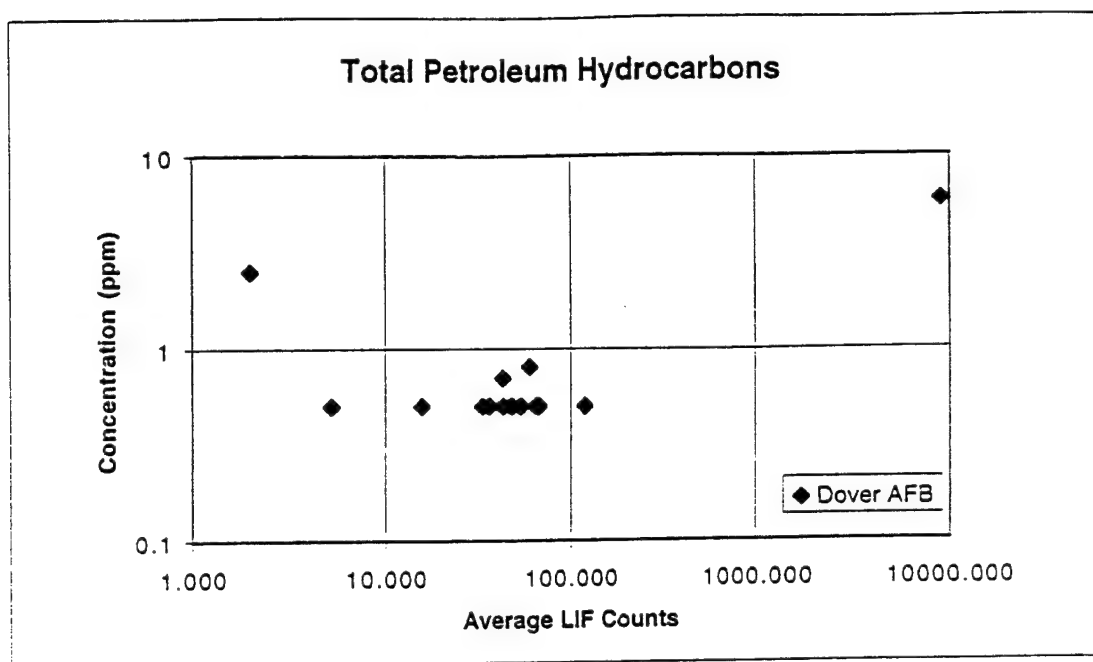


Figure 12. Total Petroleum Hydrocarbons (TPH) Versus Average Counts.

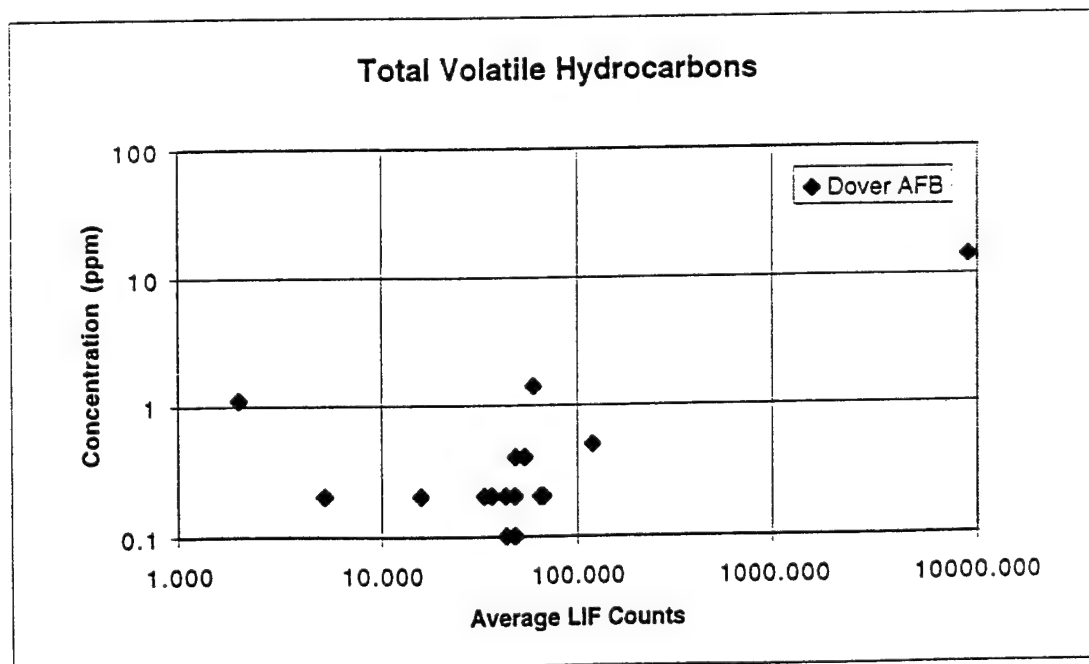


Figure 13. Total Volatile Hydrocarbons (TVH) Versus Average LIF Counts.

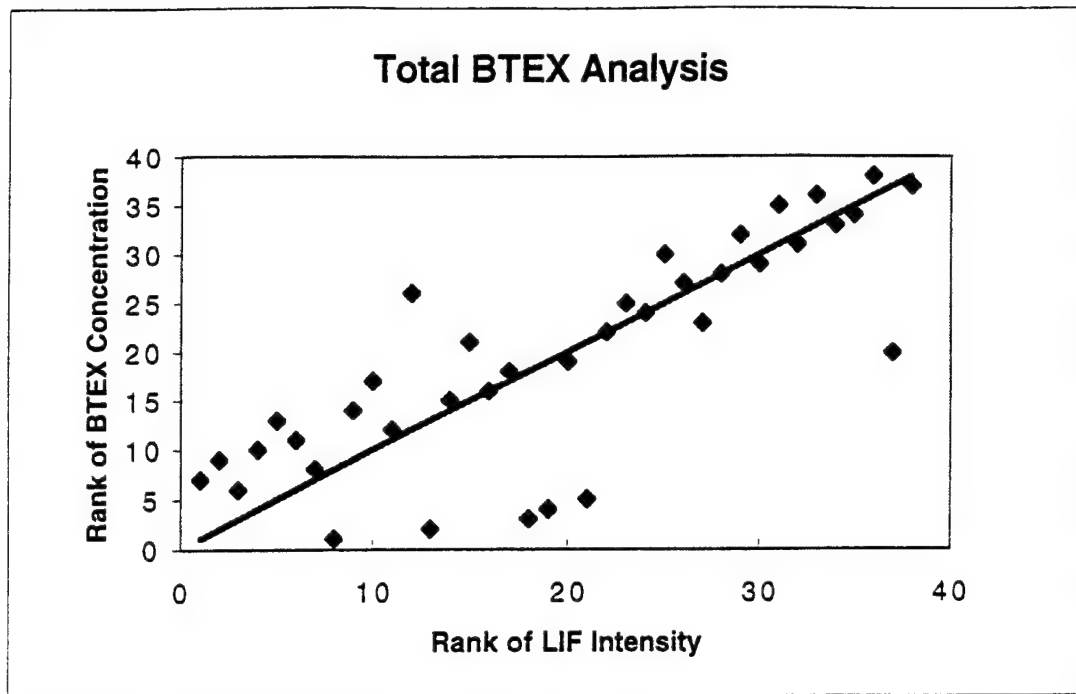


Figure 14. Rank Analysis of Total BTEX Concentration for Soil Samples from all Three Sites.

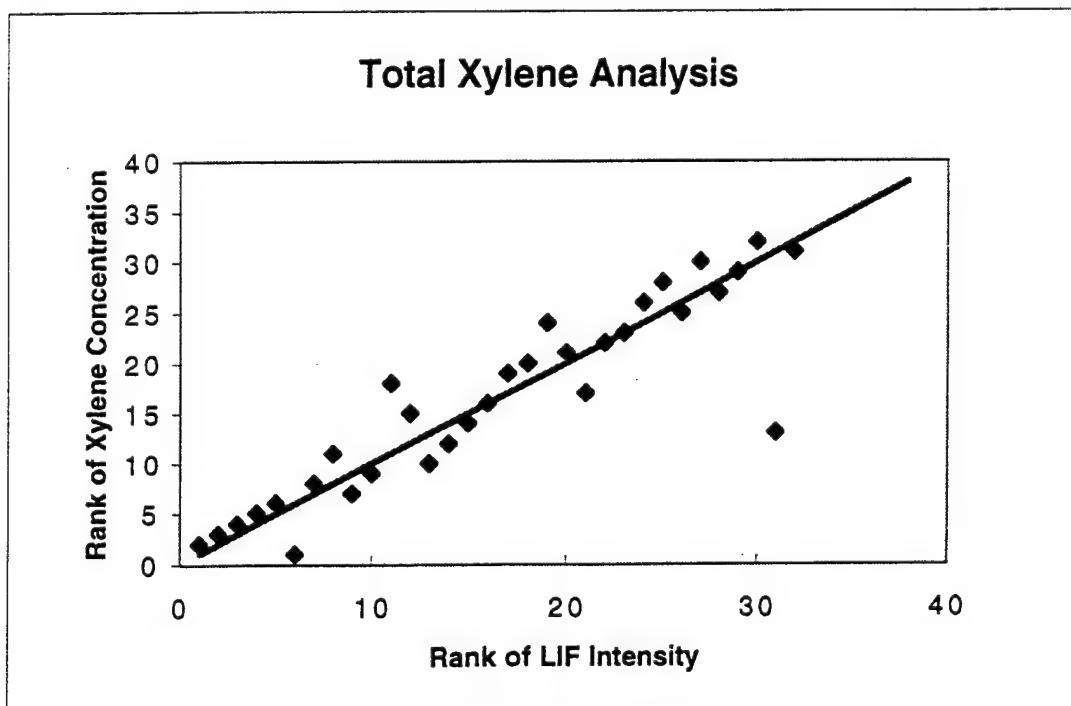


Figure 15. Rank Analysis of the Total Xylene Concentration for Soil Samples.

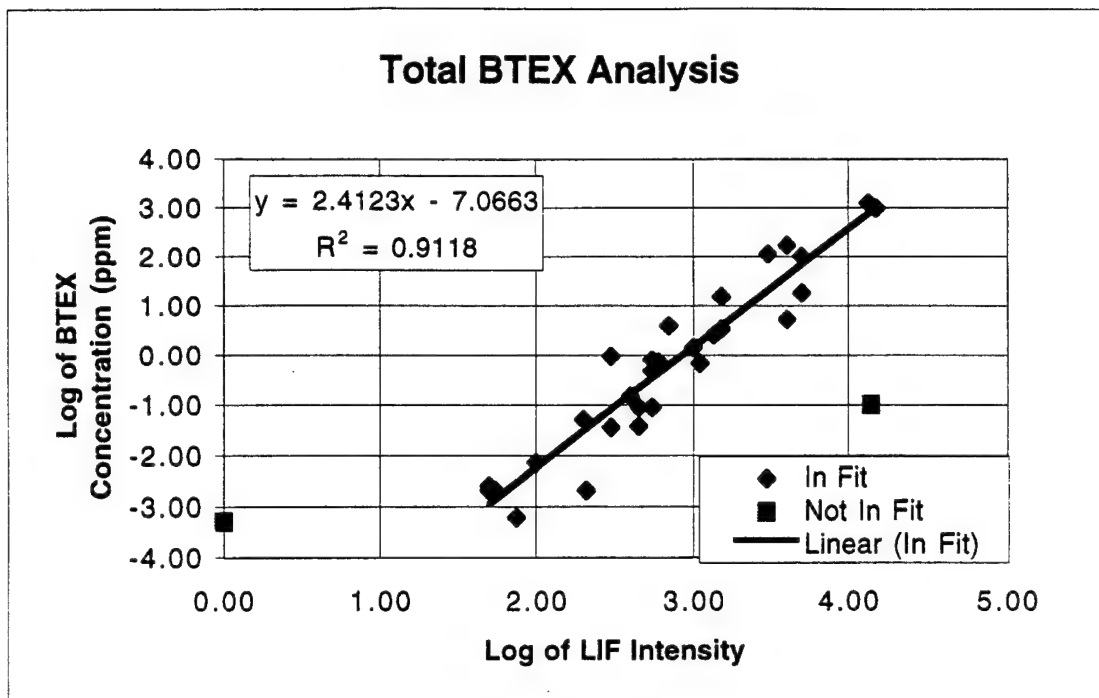


Figure 16. Comparison of Total BTEX Concentrations and LIF Response for Soil Samples from all Sites.

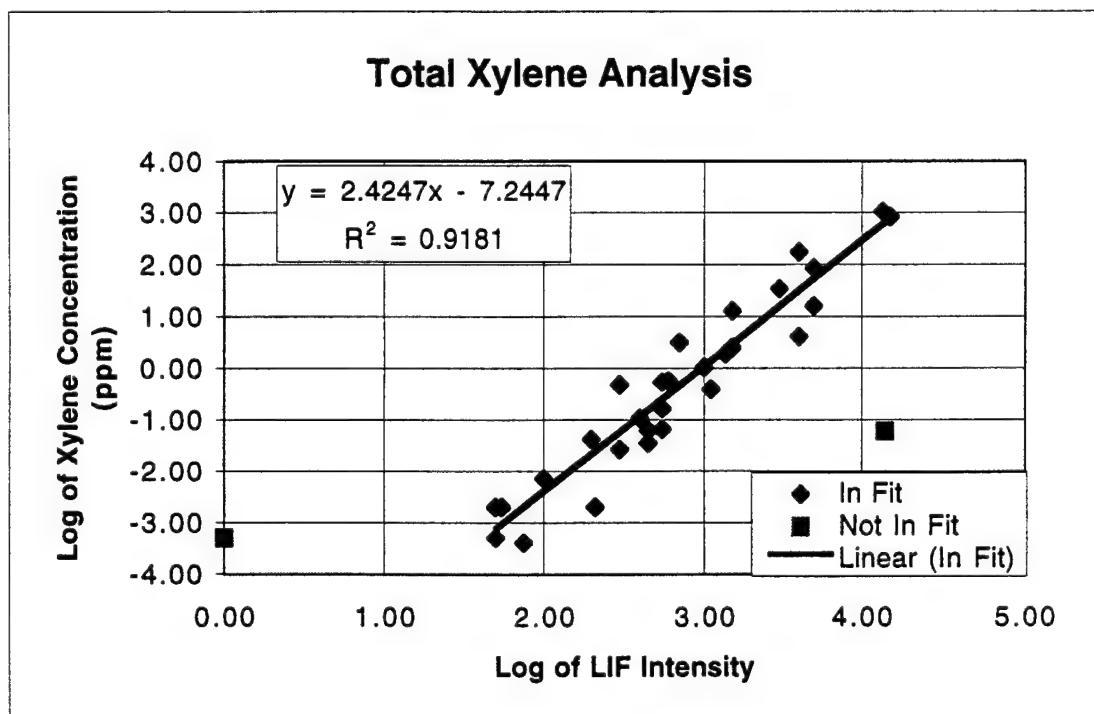


Figure 17. Comparison of Total Xylene Concentrations and LIF Response for Soil Samples from all Sites.

and 17 reflect fits that were developed for wavelengths other than the peak excitation wavelength of the contaminate; therefore, nonlinear effects are introduced.

E. WTM ANALYSIS

Wavelength time matrices (WTMs) were measured at all of the locations for which very strong fluorescence intensity was observed. They all resemble JP-4. Slight differences in their appearances are caused by distortion along the time axis at high signal levels. There is one WTM in this data set, XWTM04A(xx), that has a distinctly different shape. The maximum intensity occurs at about 355 nm (a longer wavelength than for JP-4) and the contour lines are much more extended along the wavelength axis. This response represents either a different contaminant present, or anomaly in the system response.

F. ASSESSMENT OF SOURCES OF DATA SCATTER

As with any field experiment, there are several possible sources for data scatter. Some of the scatter present during the testing at Plattsburgh, Patrick and Dover AFB's was due to large sampling intervals, effects of soil mechanics, consistency of measured parameters (i.e. were all LIF responses from the same or different contaminants), variability in the analytical chemical testing, and variability in the LIF-CPT test operating procedures. Some of these sources of scatter are controllable, while others are not and will be present during any testing program.

One major source of data scatter was the large sampling interval, sometimes as large as 3 feet. The scatter occurs as the LIF measurements were made every 1 to 2 inches, whereas the sampling interval sent to the analytical laboratory typically ranged over 1 to 2 feet. The sample volume required by the analytical laboratory was typically one quart, which would comprise 1 to 2 feet of drilling core. All this core would be mixed together and tested to determine the various chemical parameter values. If only a thin seam of the soil was contaminated, the test results may have been diluted, and not representative of the thin seam that caused the LIF response. The laboratory test results were then compared to the average LIF response measured over that interval. In the future, CPT soil sampling should be used to obtain samples from precise depths, and the smallest possible sample volume should be tested to determine contamination. The CPT soil sampling methods are more precise than traditional drilling methods for determining the sample locations, and generally have nearly 100 percent sample recovery, as opposed to 70 to 80 percent for drilling techniques.

The second improvement that can be made to reduce scatter would be a better understanding of how soil mechanics effect the LIF response, and any potential corrections that may be needed to reduce or compensate for these effects. The first step along this process was performed during the laboratory testing program phase of this project. However, this initial program has just begun to investigate the effect of soil parameters on LIF response. Key parameters that need to be evaluated in the future include the effects of soil type, soil moisture and soil compression as the CPT passes through the soil.

SECTION VI

CONCLUSIONS AND RECOMMENDATIONS

A. PROJECT OVERVIEW

The Air Force seeks efficient means to assess, remediate, and monitor petroleum contaminated hazardous waste sites at both active and decommissioned installations. Common contaminants at Air Force facilities include jet fuels such as JP-4, JP-5, and JP-8. These are common fuels stored, transferred, and consumed at bases, although other fuel spills such as heating oil, diesel fuel, and gasoline are also of concern. Integration of the cone penetrometer technique with advanced sensors such as the laser-induced fluorescence sensor has been identified as one of the most promising methods of gathering the data required to accurately and rapidly characterize the large number of Air Force sites. The CPT provides accurate in situ geotechnical information in a rapid and cost effective manner. With the adaptation of in situ geophysical and chemical sensors to the cone penetrometer probe, subsurface contamination can be mapped simultaneously. The speed and continuous nature of the information generated by LIF-CPT reduces the need for costly and invasive subsurface sampling and the installation of long term monitoring wells.

The potential for substantial cost savings realized through cone penetrometer-based environmental site investigations has fostered collaborative federal research and development efforts by the U.S. Army, Navy and Air Force in a program known as the Site Characterization and Analysis Penetrometer System (SCAPS). SCAPS generically refers to chemical sensors deployed with a cone penetrometer. Much of the SCAPS work to date employs fiber-optic-based spectroscopy with light delivered to the soil via a sapphire window "viewport" in the side of the cone. The sapphire window concept was developed and first implemented by personnel at the U.S. Army Corps of Engineers Waterways Experiment Station (WES) (Reference 1).

- To fulfill the objectives of this project, the following tasks were completed:
- Evaluation of the current state of the art and development of specifications for an improved, wavelength-tunable LIF system,
- Fabrication and integration of the LIF system in ARA's CPT truck,
- Laboratory evaluation testing,
- Preparation of Demonstration, Test and Evaluation (DT&E) Plans for Plattsburgh, Patrick/Cap Canaveral, and Dover Air Force Bases,
- Performance of the DT&E programs at each of the air bases,

- Delivery of the operations LIF system to the U.S. Army for installation in a SCAPS CPT truck.

B. SUMMARY OF LIF SYSTEM IMPROVEMENTS

Many improvements were made to the first generation LIF system to improve both the system performance and suitability for field use. System improvements performed under this effort are summarized below.

- The breadboard was reduced in size to 24 inches by 24 inches from 30 inches by 48 inches in the previous system.
- The second (Coumarin 500) dye laser was replaced with direct frequency doubled light to produce a 266 nm emission.
- All components (with the exception of the monitor of the laser control computer), are packaged into a single unit approximately 48 inches L by 24 inches W by 36 inches H,
- The pulse repetition rate was increased from 10 to 50 Hz.
- The Nd:YAG pump laser, including power supply, was downsized from approximately 13 cubic feet volume to 3.25 cubic feet.
- The necessity for 208-240 V power was eliminated; only standard 110 line voltage is now required.
- The digital oscilloscope was upgraded to the TDS 620. This improves signal to noise ratio due to the elimination of interleaved sampling at short time bases.
- The photomultiplier tube of the first generation system was replaced with a smaller, less costly model.
- The stability of frequency doubling process was improved substantially by temperature control of the doubling crystal.
- A new shock mounting system was developed to allow transport of the laser system while installed in the cone penetrometer truck.
- More tests and calibration procedures were built into the system. For example, the optimization of the doubling crystal position is now fully automated, eliminating operator manipulations.
- Automated power measurements were added and recorded for normalization in during post processing.
- Improvements were made in the downhole optics. Repairs and alignment can now easily be made in the field. These improvements included addition of an optical connector at the CPT probe to facilitate repair of both the CPT probe and optical probe, and inclusion of downhole optical filters that reduce the optical background. Additional improvements

include reducing the number of optical fibers from 6 to 2, and decreasing the fiber size, both of which reduce the cost of the LIF system without degradation of the system performance.

- Development of a method to place well points with the CPT that were used to obtain water samples as part of a monitoring program.

C. SUMMARY OF DT&E FIELD TESTING

During the three DT&E programs, several advantages of the AFSCAPS system were demonstrated, which include:

- CPT is minimally invasive and generates no drilling waste.
- CPT is a rapid test and greatly reduces cost.
- Continuous profiling of soil stratigraphy and contamination can be made in which even the thinnest soil layers can be detected. For many sites, thin sand seams carry the majority of the contaminants and are difficult to locate with conventional drilling techniques.
- Real-time determination of soil stratigraphy, water table depth and degree of contamination can be made with the LIF-CPT. These data are used to optimize location of the next sounding. On full-scale investigations, this capability can greatly reduce the time required to characterize a site, and result in a more thorough investigation resulting in a greater understanding of the spatial distribution of the contaminant that is possible with conventional drilling and sampling methods.

The LIF and chemical analysis data agree well qualitatively and quantitatively. Correlations were made between the limited chemical data and the LIF data that allowed prediction of the total bTEX and total xylene contamination. Analysis of the data indicates that the background limit of LIF-CPT probe is independent of soil type but may have a weak dependency on moisture content. Based on the data presented and analysis of data from other profiles in relatively clean areas, the background limit of the LIF-CPT probe as configured is roughly 50 counts. Any data obtained below this limit must be interpreted as below the system detection limit. There are still open questions regarding the response of the LIF system in different soils. At some locations, the LIF response indicates contamination in clayey layers; yet at others, where sensory inspections of soil samples indicate fuel contamination, the LIF response does not indicate any contamination. Sufficient chemical data was not available to answer these questions or fully validate the LIF system.

D. RECOMMENDATIONS FOR FUTURE WORK

As with any development program, there are several improvements that can be made. The area that requires the most work is the analytical sampling program, which supported the development of correlations to the LIF. The data set available was insufficient to evaluate the influence of soil type on the LIF, and no chemical data was available for the wavelength monitored during the CPT push. For future testing, it is highly recommended that on-site field analytical testing be conducted using portable instruments, such as the BUCK model 404 for performing EPA Method 418.1. Soil samples should be obtained at exactly the same location as the LIF-CPT push by overcoring the push location. The analytical testing should concentrate on soil tests.

In addition, laboratory studies should be performed to evaluate the effects of soil type, soil moisture content, and the compression effects experienced near the CPT probe have on the LIF response. Based upon the field testing during the demonstration, soil type was identified as having a major influence on the LIF response. Moisture content was identified as having a minor effect based on limited data and additional study as warranted. These types of studies would also assist the development of standard operating and calibration procedures. Once these procedures are in place and the reliability studies have been performed, the EPA regulator may be able to approve this technology.

Finally, improvements to the system to enhance the detection limit are needed. Assessment of the actual detection limit of the new system has been difficult but appears to be at least as good as the previous system and possibly slightly better. Methods are needed for detecting concentrations in the 500 ppb level range in soils. The LIF technique has potential to reach these levels if the soil effects can either be eliminated or compensated for and the system performance improved. A couple of system improvements that should be investigated are increased power on the sample, and larger sample exposure area. If lower detections are achieved, then the LIF technology may receive greater usage, further reducing site investigation costs.

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